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Phthalates and Polybrominated Diphenyl Ethers in Retail Stores

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Phthalates and Polybrominated Diphenyl Ethers in Retail Stores

by

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Dedication

To my mom and sister, and to my Luna.

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Abstract

Phthalates and Polybrominated Diphenyl Ethers in Retail Stores

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Retail stores are an environment with a rich diversity of toxic chemicals typically found in consumer products. Among these chemicals, semi-volatile organic compounds (SVOCs) are an important class with great health concerns. Phthalates and polybrominated diphenyl ethers (PBDEs) are high production volume SVOC chemicals pervasively used in plastics and other consumer products. Exposure to them may cause serious adverse health effects, including endocrine disruption. They, however, have not been widely studied in retail environments. In this study, indoor air samples were collected from 15 retail stores in Austin, TX and University Park, PA. Some of these stores were revisited on different temperate seasons to account for weather variability. Indoor concentrations of the most ubiquitous pollutants were correlated with several building characteristics, including retailer type, temperature, and building use characteristics. Collected data shows a wider variety of phthalates and PBDEs, as well as higher indoor airborne concentrations for large department stores as compared to grocery stores, which typically have fewer sources in comparison.

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Chapter 1: Introduction

Indoor environments have gotten an increased attention within the last few decades (Weschler 2009). People spend more than 87% of their time indoors (Klepeis et al. 2001), and the chemicals found in this environment can have multiple effects on human health. Modern trends show that while some pollutants have decreased in concentration in the last 50 years (lead, mercury, volatile aromatics, chlorinated pesticides, etc.), some others have been found at higher levels than in decades before. A group of chemicals that have increased their levels indoors in recent years are semi-volatile organic compounds (SVOCs). This group of compounds includes phthalate plasticizers and polybrominated diphenyl ethers (PBDEs), which are added to consumer products to alter their physical properties and to reduce material combustibility, respectively (Carlsson et. al 1997, Wang et. al 2010). These are often found at mass percentage levels in the order of tenths. For example, polyvinyl chloride (PVC) flooring typically contains 30% to 40% by mass of phthalate plasticizers (Claussen et al. 2004, Bornehag et al. 2005). When released to the gas phase, these low vapor pressure ($<10^{-10}$ mmHg) compounds adsorb to settled dust, interior surfaces and suspended particles (Weschler & Nazaroff 2010).

Production of plasticizers grew at an average annual rate of 4.7% from 2005 to 2008 (IHS 2009). Global capacity utilization decreased significantly from 71% in 2005 to 62% in 2008 as a result of increased capacity and weak demand caused by the global recession. Although world demand increased during 2005–2007, it weakened considerably during 2008 in most regions, wiping out most volume gains since 2005. Phthalate plasticizers accounted for almost 86% of world consumption of plasticizers in 2008 and it is forecasted that they will account for the same number until at least 2012. The global production rate of phthalate plasticizers has increased from 2.5 million tons/year to 6 million tons/year within a decade (Cadogan et al. 1996, SRI 2007). Phthalates are suspected of having carcinogenic and teratogenic effects. One of the biggest concerns is the possible toxic effects it might have in humans regarding development and reproduction (Bornehag et al., 2004, David, 2004). Early exposure to phthalates could be a key

mechanism in the pathology of allergic asthma in children (Bornehag and Nanberg 2010), and reproductive disorders (Latini et al 2004). *In vivo* and *in vitro* studies also supported the adjuvant effects on basic mechanisms in allergic sensitization by several phthalates (Larsen et al. 2004 and 2007, Yang et al. 2008, Bornehag et al. 2010). Phthalates have been detected in a wide variety of indoor environments, including residential studies (Rudel 2003 and 2010, Otake et al. 2001, Fromme et al. 2004, Kanazawa et al. 2010, Adibi et al. 2008). In the children's total exposure to persistent pollutants (CTEPP) study, concentrations of two phthalates were detected in residential air and house dust, and on a range of interior surfaces and dermal wipe samples. The measured phthalate concentrations were amongst the highest of any of the target compounds (including pesticides, PAHs and PCBs) and were generally higher on human skin than on all other surfaces (Xu et al. 2009 and 2010).

PBDEs have found their way into indoor environments via plastics, textiles, foams, electronic equipments, and other consumer products that have been associated with them (Batterman et al. 2009). These compounds are not chemically bound additives mixed into polymers to reduce its combustibility (de Wit, 2002). Approximately 56,418 metric tons (MT) of PBDEs were produced worldwide in 2003, the latest reporting year, with between 40,000 and 67,000 MT/year produced between 1999 and 2002. (USEPA 2010). These compounds may leach into the airborne from products that enter the indoor environment. PBDEs are persistent in the environment, and bioaccumulate in biota and humans (Allen et al. 2007). The body burden of this set of compounds has increased over several decades, and varies significantly from one region to another (Noren 2000). People living in the US have been reported to have some of the highest PBDE concentrations (Hites 2004). The toxicity of these compounds is still highly debated (WHO 2007), and inhalative, oral, or dermal intake is being evaluated. PBDEs, like phthalates, are also endocrine-disrupting chemicals (WHO 2007). Studied have shown that PBDE compounds affected cell migration and differentiation by interfering with thyroid hormone signaling, an endocrine-disrupting effect that could be associated with additional impacts throughout a person's life. (Betts 2010). Prenatal exposure to PBDEs is associated with

adverse neurodevelopmental effects in young children (Schreiber et al. 2010), as children with higher concentration of PBDEs in their umbilical cord blood had lower IQ points (5.5~8.0) when tested in verbal and full IQ scores.

An understudied indoor environment considering the energy, occupant risk and economic implications associated with poor indoor air quality is that of retail stores. Over 15 million people work in the retail sector in the U.S. (NRF 2010). Retail stores account for approximately 28% of commercial buildings and utilize 22% of commercial floor space (Diamond 2001). Despite of this, little has been done to characterize concentrations of indoor pollutants. Two studies (Hartman et al. 2004, Wu et al. 2008) have shown evidence that plasticizers and flame-retardants are found in retail environments. Hartman et al. (2004) used polyurethane foam (PUF) plugs to collect air samples and measure concentrations of eight organophosphates in car, retail and office environments in and around Zurich, Switzerland. The retail environments included electronics and furniture stores. Tributyl phosphate (TBP), Tris (2-chloroethyl) phosphate (TCEP) and Triphenyl phosphate (TPP) were found in all of the retail stores. Tris(2-chloro-isopropyl)phosphate (TCPP) was found in furniture stores, but not in electronics stores, and Tris(1,3-dichloroisopropyl) phosphate (TDCP) was not found in any of the locations studied. Wu et al. (2008) used multi-bed sorbent tubes with a primary bed of Tenax-TA sorbent backed with a section of Carbosieve III to capture air samples and measure Diethyl Phthalate (DEP), as well as several VOC concentrations in 37 small- and medium-sized commercial buildings distributed across different sizes, ages, uses, and regions of California. DEP was found in all seven of the retail sites, with mean concentrations slightly higher than those found in residences (Rudel et al., 2010).

In this study, a total of 14 stores (seven in Texas and seven in Pennsylvania), were visited to determine airborne and dust phase concentrations of 6 phthalate esters and 14 PBDEs, with several sites visited more than once. Airborne concentrations were measured with the use of sorbent and PUF tubes. Dust concentrations were measured by replacing the filter from

recirculating rooftop air handling units for approximately 30 days, and the dust collected during that time period was extracted and analyzed.

Relationships between the two different types of SVOC phases were analyzed to determine the strength of the link between gas and dust concentrations. The study is also aimed at determining possible source and fate mechanisms by analyzing building type materials, ventilation rates and temperatures also observed as part of the project, and correlating them with the quantified concentrations.

Chapter 2: Methods

The following sections describe the sample of retail buildings that were investigated, the general methodology for each field visit, the specific approaches for collection and analysis of samples, and the quality assurance approach that was used for each measurement.

2.1 BUILDINGS SAMPLES

Fourteen retail buildings were visited for this study; 7 located in Austin, Texas, and 7 in the state of Pennsylvania. These buildings were the same as the ones visited for the ASHRAE RP-1596 project, a thorough study on the ventilation and indoor air quality in retail stores. Table 1 describes the sample in more detail. 8 different store categories were visited. A site identification code was used for each store where the first letter is the store type (H = home improvement, M = general merchandise, F = Furniture, E = Electronics, O = Office, G = mid-sized grocery, and S = small grocery), the second letter is a unique brand identifier, and the third character indicates whether the site was located in Pennsylvania (P) or Texas (T). The labeling is consistent with the one used for the ASHRAE RP-1596 report. The fourth column indicates how many times the store was visited. The fifth and sixth columns are the sampling location and period, respectively.

Two general merchandise stores (MbP and MbT) were tested in all four seasons of the year, four stores were tested in both summer and winter, and seven stores were tested only once. Additionally, two different tests were done at one general merchandise store in Texas (MiT). During the first test, the ventilation rate was increased to its maximum allowed capacity. For the second one, the ventilation was returned to its typical operation. The test at the higher ventilation rate is generally excluded from summary data, except on Section 4.3, where the effect of ventilation on SVOC concentrations is analyzed and discussed.

Category Label	Type	Site	Times Visited	Location	Months Tested
I	Home improvement	HaP	2	Pennsylvania	May Nov
		HaT	1	Texas	Jun
II	General merchandise	MbP	4	Pennsylvania	Sep Jan May Jul
		MbT	4	Texas	Jul Oct Feb Apr
		MiP	1	Pennsylvania	Apr
		MiT	1*	Texas	Apr
III	Electronics	EgP	2	Pennsylvania	Feb Jun
IV	Office supply	OhT	1	Texas	May
V	Furniture	FfP	1	Pennsylvania	Mar
		FfT	2	Texas	Oct Feb
VI	Grocery (mid-size)	GeP	1	Pennsylvania	Jul
		GeT	2	Texas	Sep Jan
VII	Grocery (small)	ScP	1	Pennsylvania	Aug
		SdT	1	Texas	Aug

***- Intervention site**

Table 1: Summary information about test locations.

2.2 SAMPLING APPROACH

Indoor air samples were collected in Austin, TX and University Park, PA. These were chosen to account for different source materials, as well as reflect a wide range of building materials.

2.2.1 Sampling approach

2.2.2.1 Airborne Sampling Methods

The detailed field sampling procedures for airborne sampliment measurements are discussed in Appendix A. For the first seven tests, sorbent tubes (1/4" OD x 3-1/2" length, 250 mg of sorbent) packed with Tenax TA were used. For Tests 14, 15 and 17-24, polyurethane foam (PUF) sample tubes (22 X 100 mm size, 1-section, 76 mm sorbent) with a glass fiber filter were used. The air sample collection system consisted of a calibrated air pump, PTFE tubing and two sorbent tubes connected in series, referred to as a sample train. Prior to each test, the sorbent

tubes were analyzed using thermal desorption followed by gas chromatograph and mass spectrometry to ensure no phthalates were present before sampling. After testing the background level, the sorbent tubes were placed in a zip bag and transported in a cooler with temperatures below 4 °C (~39 °F) before and after sampling. The sorbent tubes were stored at temperatures below 4 °C (39 °F) for 2 days before analysis. The sample pumps were calibrated for a nominal volumetric flow rate of ~75 ml/min (0.16 ft^3/hour), with the exception of test 01 and test 02, where a volumetric flow rate of ~110 ml/min (0.23 ft^3/hour) was used. The sampling time for all air samples was ~48 hrs, with the exception of Test 1 and Test 2, with 12 and 24 hrs, respectively, producing sampling volumes of 216 liters (7.6 f ft^3). Once sample collection was completed, the flow rate through the sample system was validated using a calibrated volumetric flow meter and the sorbent tubes were stored in a protective casing wrapped in aluminum foil and stored in a refrigerator to maintain a storage temperature below 4 °C (39 °F).

For PUF sampling tubes, the sampling PUF, filter and container were pre-cleaned with Hexane by sonication. PUF tubes were wrapped in aluminum foil and sealed in a zip bag before and after sampling. The sample pump for the sample collection system was calibrated for a nominal volumetric flow rate of 25 L/min (0.88 ft^3/min). The sampling time for all air samples was 48 hrs, producing sampling volumes of 72 m^3 (2,543 ft^3). Once sample collection was completed, the flow rate through the sample system was validated using a calibrated volumetric flow meter and the PUF tube was stored at a temperature below 4 °C (39 °F).

2.2.2.2 Dust Sampling Methods

Immediately following the field investigation, clean HVAC filters (MERV 7-8) were installed in at least one air handling unit. If possible the air handling units for testing were selected with outdoor air dampers closed and located away from interior doors. The HVAC filters at a given retail site were installed for approximately 30 days. After completion of testing, the filters were removed and placed into a loosely sealed bag. All of the sampled filters from Pennsylvania were shipped to Texas immediately following the required sampling time. For

shipping, the filters were wrapped in a static shielding bag and shipped overnight in a cooled, insulated container. The filters retrieved in the Austin area were stored for one night in a 4 ºC (39.2 ºF) room.

2.3 LABORATORY SAMPLE ANALYSIS

2.3.1 Sorbent Tubes

Indoor air SVOC samples for the first seven test sites were collected using sorbent tubes packed with Tenax® TA. Prior to analysis, the sorbent tubes were returned to their original containers and stored in a refrigerator at a temperature of ≤4°C (39 °F). Analysis of sorbent tubes was done at the University of Texas at Austin. A Thermal Desorption Unit (Turbomatrix 650 ATD) was used preliminary to the GC-MS analysis for air samples. A GC-MS (Agilent 7890A) system was operated in using a 5:1 split injection, using a 30m DB-5ms column. The oven temperatures were programmed from 80 °C for 0.5 min, ramp 20 °C/min for 8.5 min, then ramp 30 °C for 2 min, hold 9 min.

2.3.2 PUF tubes

Indoor air SVOC samples for test sites 15, 16, 17, 19, 20, 21, 22 and 23 were collected using PUF cartridges. Prior to analysis, the PUF cartridge was returned to their original containers and stored in a refrigerator at a temperature of ≤4°C (39 °F). The SVOCs collected on the PUF cartridges were extracted and concentrated for analysis. PUF cartridges were placed into a 150ml volumetric glass flask along with 100 ml of hexane and sonicated for 2 hours and 15 minutes. The volume of the extracted samples was reduced to 5 mL in a rotary evaporator. Finally, a nitrogen purge was used to further reduce the sample volume to approximately 150 µL. Following the nitrogen purge, the sample was weighed and the density of the hexane (0.672 g/mL), was used to calculate final sample volume. The detailed procedure for PUF extraction can be found in Appendix B. A GC (Agilent 7890A) coupled to a FID (for phthalate analysis) and a µECD (for PBDE analysis) using a DB-5ht columns was utilized. For phthalates, A GC-FID (Agilent 7890A) system was operated using a 4:1 split injection. The inlet temperature was

set at 275°C and a constant column flow was set at 1.2 ml/min. The oven temperatures were programmed from 120°C for 2 min, ramp 12°C/min for 15 min, hold 3 min, then ramp 20°C/min for min, hold 2 min. The detector was set at 320°C. For PBDEs, A GC-μECD (Agilent 7890A) system was operated using a pulsed splitless injection with an injection pulse pressure at 30 psi until 1 minute and a purge flow to split vent of 50 mL/min at 1.5 min. The inlet temperature was set at 325°C and a constant column flow was set at 1.1978 ml/min. The oven temperatures were programmed from 80°C for 0.5 min then ramp 20°C/min for 13.5 min, hold 2 min. The detector was set at 360°C.

2.3.3 Filter Dust

Filter dust SVOC samples were collected from all test sites by replacing the filter of at least one of the rooftop HVAC units. Sections of the filter were taken, with the size varying depending on the filter media. The extraction method was identical to the one of PUF tubes, with the exception of reducing it to a sampling volume of approximately 1ml due to a higher chemical loading into the solvent. The analysis for the dust was identical to the one of PUF tubes.

2.4 CHEMICALS AND MATERIALS

Diethyl Phthalate (DEP), Dimethyl Phthalate (DMP), Di-n-butyl Phthalate (DBP), ButylBenzyl Phthalate (BBP), Di(2-ethylhexyl) Phthalate (DEHP) and Di-n-octyl Phthalate (DoP) were purchased from Absolute Standards. 2,2',4,-Tribromodiphenyl ether (BDE-17), 2,4,4'-Tribromodiphenyl ether (BDE-28), 2,2',4,4'-Tetrabromodiphenyl ether (BDE-47), 2,3',4,4'-Tetrabromodiphenyl ether (BDE-66), 2,3',4',6-Tetrabromodiphenyl ether (BDE-71), 2,2',3,4,4'-Pentabromodiphenyl ether (BDE-85), 2,2',4,4',5-Pentabromodiphenyl ether (BDE-99), 2,2',4,4',6-Pentabromodiphenyl ether (BDE-100), 2,2',3,4,4',5'-Hexabromodiphenyl ether (BDE-138), 2,2',4,4',5,5'-Hexabromodiphenyl ether (BDE-153), 2,2',4,4',5,6'-Hexabromodiphenyl ether (BDE-154), 2,2',3,4,4',5',6-Heptabromodiphenyl ether (BDE-183), 2,3,3',4,4',5,6-Heptabromodiphenyl ether (BDE-190), Decabromodiphenyl ether (BDE-209) were purchased from AccuStandard.

Tenax TA tubes (catalog #226-357), Sorbent PUF tubes (catalog #226-126) and personal air pumps (catalog# 224-PCXR4) were purchased from SKC. High flow air pumps (catalog #APB-504000) were purchased from Buck LTD.

Chapter 3: Results

3.1 AIR SAMPLING

We collected SVOCs indoor air samples on sorbent tubes packed with Tenax ® TA tubes to measure phthalates for the first seven tests, then later switched to tubes with polyurethane foam (PUF) for Tests 14-24 (except 16 and 18) to also measure polybrominated diphenyl ethers (PBDE) concentrations. The detailed sampling procedures for these measurements are discussed in Section 2.2. Section 3.1.1 contains the results for phthalates, and Section 3.1.2 contains the results for polybrominated diphenyl ethers (PBDEs).

3.1.1 Phthalates

Integrated mass concentrations for six phthalates were measured indoors during the 48-hour permanent sampling event. Table 2 lists the summary statistics for indoor phthalate concentrations in the airborne phase.

Figure 1 contains a bar chart for indoor mass concentration by site. The bar height represents the average of replicate samples (when available). The uncertainty associated with phthalate measurements is the relative variance between duplicate samples and the overall uncertainty for the analytical procedure explained in Appendix C. It should be noted that we monitored indoor airborne phthalate concentrations from a fixed location in each site because of electrical power requirements. The samples may not be representative of the air sampled by other instruments during the mobile sampling event.

The average (±SD) and median indoor air concentrations for the sum of the six phthalates across all sites are 0.63 ± 0.48 $\mu g/m^3$ and 0.46 $\mu g/m^3$, respectively. The sites with the highest phthalate indoor air concentrations are ScP (1.83 $\mu g/m^3$) and FfT2 (1.31 $\mu g/m^3$). The sites with the lowest phthalate indoor air concentrations are GeP (0.09 $\mu g/m^3$) and EgP2 (0.14 $\mu g/m^3$).

Category Label	Test IDs	Site	Concentration (µg/m3)					
			DMP	DEP	DBP	BBzP	DEHP	DoP
I	1	HaP1	0.046	0.200	0.153	<d.l.	0.054	0.006
	2	HaT	<d.l.	0.173	0.185	0.013	0.392	0.027
II	3	MbT1	0.063	0.159	0.150	<d.l.	0.087	<d.l.
	19	MbT4	<d.l.	0.074	0.121	<d.l.	0.104	<d.l.
	7	MbP1	0.445	0.438	0.196		0.092	
	17	MbP3	0.009	0.076	0.138	0.088	0.071	0.005
	22	MbP4	0.808	0.105	<d.l.	0.008	0.010	<d.l.
	23	MiP	<d.l.	0.174	0.071	<d.l.	0.052	<d.l.
	24	MiT	0.008	0.083	0.071	0.056	0.021	<d.l.
III	14	EgP1	0.095	0.043	0.048	0.099	0.230	0.096
	20	EgP2	<d.l.	0.007	0.061	0.013	0.052	0.004
V	15	FfT2	0.048	0.181	0.563	0.052	0.437	0.025
VI	21	GeP	<d.l.	0.013	0.051	0.002	0.024	<d.l.
	6	GeT1	0.031	0.236	0.051	0.039	0.071	<d.l.
VII	4	ScP	0.028	0.237	1.428	0.100	0.037	<d.l.
	5	SdT	0.021	0.203	0.136	0.049	0.264	<d.l.
		Average	0.146	0.150	0.228	0.047	0.125	0.027
		Median	0.046	0.166	0.136	0.049	0.071	0.016
		Stdev	0.252	0.108	0.355	0.036	0.133	0.035
		Max	0.808	0.438	1.428	0.100	0.437	0.096

Table 2: Summary statistics of indoor air phthalate concentrations

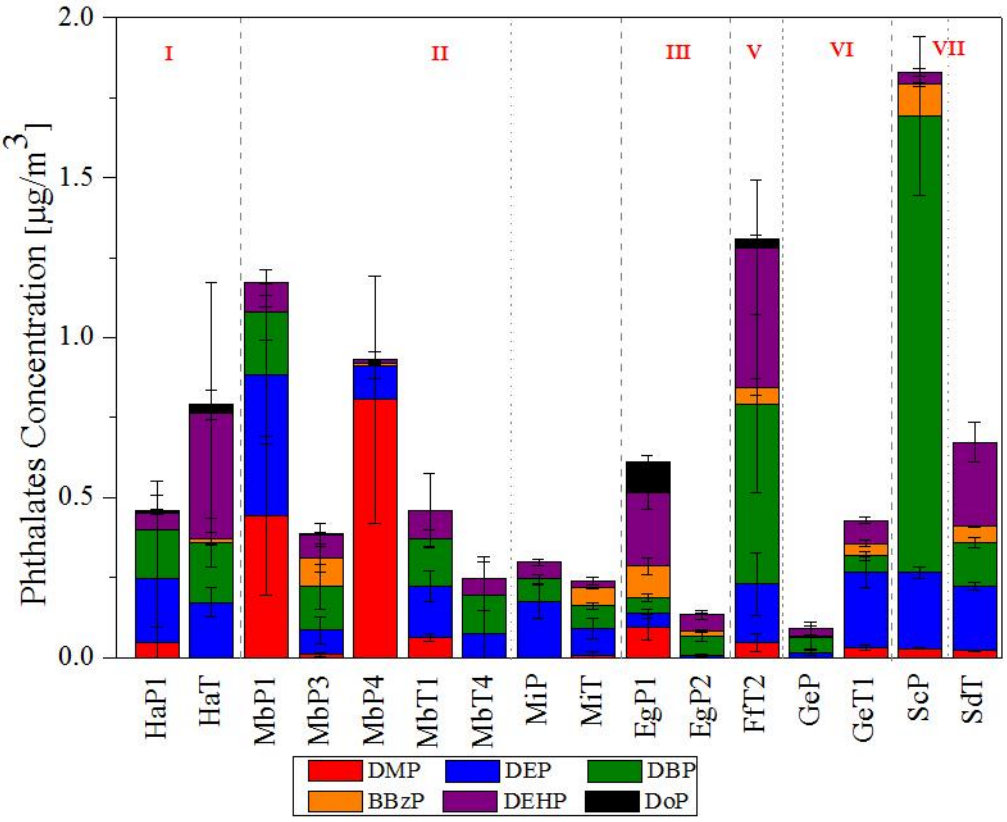

Figure 1: Phthalate indoor mass concentration in the airborne phase by site

3.1.2 Polybrominated diphenyl ethers:

Integrated mass concentrations for fourteen PBDEs were measured indoors during the 48-hour permanent sampling event indoors. Table 3 lists the summary statistics of PBDE indoor concentrations in the airborne phase.

A bar chart for indoor mass PBDE concentration by site is shown in Figure 2. The bar height represents the average of replicate samples (when available). The uncertainty associated with PBDE measurements is accounted for the relative variance between duplicate samples, and the overall uncertainty for the analytical procedure explained in Appendix C. Similarly to phthalates, we monitored indoor airborne PBDE concentrations from a fixed location in each site.

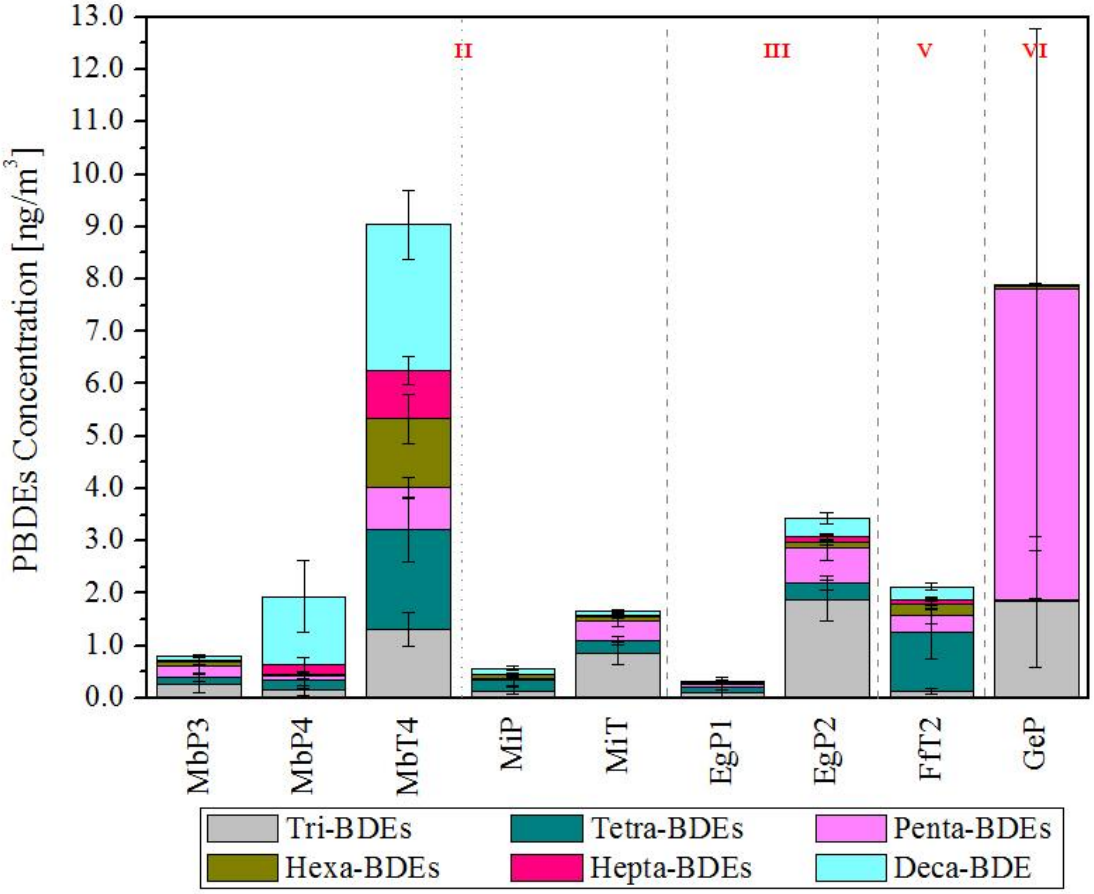

Figure 2: PBDE indoor mass concentration in the airborne phase by site

Category Label	Test IDs	Site	Concentration (ng/m^3)													
			BDE-17	**BDE-28**	**BDE-71**	**BDE-66**	**BDE-47**	**BDE-100**	**BDE-99**	**BDE-85**	**BDE-154**	**BDE-153**	**BDE-138**	**BDE-183**	**BDE-190**	**BDE-209**
II	19	MbT4	0.459	0.855	0.662	0.382	0.871	<d.l.	0.254	0.537	0.454	0.532	0.328	0.277	0.645	2.786
	17	MbP3	0.211	0.045	<d.l.	0.101	0.037	0.040	0.130	0.054	0.026	0.027	0.029	0.007	0.014	0.083
	22	MbP4	0.073	0.077	0.074	0.087	0.026	0.036	0.068	<d.l.	0.005	<d.l.	0.017	0.019	0.159	1.301
	23	MiP	0.079	0.064	0.159	0.038	<d.l.	0.038	<d.l.	<d.l.	0.039	0.018	0.017	0.006	<d.l.	0.111
	24	MiT	0.035	0.813	0.134	0.121	<d.l.	0.144	0.201	0.040	<d.l.	0.048	0.015	<d.l.	0.025	0.192
III	14	EgP1	0.028	0.086	0.030	0.047	0.024	0.008	0.034	0.011	0.005	0.007	0.004	0.005	0.003	0.031
	20	EgP2	<d.l.	1.869	0.110	0.175	0.057	0.030	0.268	0.369	0.057	0.036	<d.l.	0.029	0.082	0.354
V	15	FfT2	0.077	0.069	1.051	0.036	0.029	0.031	0.102	0.176	0.181	0.042	0.002	0.050	0.046	0.238
VI	21	GeP	1.647	0.199	<d.l.	<d.l.	0.047	0.025	5.768	0.114	0.021	0.026	0.015	<d.l.	0.040	<d.l.
		Average	0.33	0.45	0.32	0.12	0.16	0.04	0.85	0.19	0.10	0.09	0.05	0.06	0.13	0.64
		Median	0.08	0.09	0.13	0.09	0.04	0.03	0.17	0.11	0.03	0.03	0.02	0.02	0.04	0.22
		StDev	0.55	0.62	0.39	0.11	0.32	0.04	1.99	0.20	0.15	0.18	0.11	0.10	0.22	0.96
		Max	1.65	1.87	1.05	0.38	0.87	0.14	5.77	0.54	0.45	0.53	0.33	0.28	0.64	2.79

Table 3: Summary statistics of indoor air PBDE concentrations.

The average and median values for the sum of the 14 PBDEs concentration across all sites were 1.94 ± 3.05 ng/m^3 and 3.10 ng/m^3, respectively. The sites with the highest PBDE concentration are MbT4 (9.04 ng/m^3) and GeP (7.90 ng/m^3). The sites with the lowest PBDE concentrations are EgP1 (0.32 ng/m^3) and MiP (0.57 ng/m^3).

3.2 DUST SAMPLING

We collected SVOCs filter dust samples on tillers collected from recirculating rooftop units. The detailed sampling procedures for these measurements are discussed in Section 2.2.2. Section 3.2.1 contains the results for phthalates, and Section 3.2.2 contains the results for polybrominated diphenyl ethers (PBDEs).

3.2.1. Phthalates

Mass concentrations for six phthalates were measured from filters collected from recirculating rooftop units. The extraction analysis is described in more detail in Section 2.2.2.2. Table 4 lists the summary statistics for indoor phthalate concentrations in the airborne phase.

Figure 3 contains a bar chart for filter dust mass concentration by site. The bar height represents the average of replicate samples (when available). The uncertainty associated with phthalate measurements is the relative variance between duplicate samples and the overall uncertainty for the analytical procedure explained in Appendix C.

The average (±SD) and median concentration for the sum of the six phthalate across all sites are 1,354 ± 1,840 µg/g and 613 µg/g respectively. The sites with the highest filter dust phthalate concentrations are ScP (6,925 µg/g) and MbP2 (5,186 µg/g). The sites with the lowest filter dust phthalate concentrations are MbT4 (below detection limits for all compounds), MbT3 (15 µg/g) and GeT1 (15 µg/g).

Category Label	Test IDs	Site	Concentration (μg/g)					
			DMP	DEP	DBP	BBzP	DEHP	DoP
I	1	HaP1	<d.l.	<d.l.	<d.l.	<d.l.	192	<d.l.
	9	HaP2	<d.l.	6	16	35	65	22
	2	HaT	<d.l.	<d.l.	<d.l.	<d.l.	128	39
II	3	MbT1	<d.l.	<d.l.	8	<d.l.	78	<d.l.
	10	MbT2	<d.l.	<d.l.	<d.l.	<d.l.	52	<d.l.
	12	MbT3	<d.l.	<d.l.	<d.l.	<d.l.	15	<d.l.
	19	MbT4	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
	7	MbP1	<d.l.	<d.l.	616	152	4,187	231
	13	MbP2	<d.l.	37	100	80	700	47
	17	MbP3	<d.l.	25	347	343	2,658	106
	22	MbP4	<d.l.	49	172	450	1,339	150
	23	MiP	<d.l.	72	219	36	294	49
	24	MiT	<d.l.	152	57	543	166	38
III	14	EgP1	<d.l.	121	635	240	1,101	323
	20	EgP2	<d.l.	<d.l.	218	900	2,283	343
IV	18	OhT	<d.l.	<d.l.	<d.l.	<d.l.	57	<d.l.
V	16	FfP	<d.l.	591	574	178	655	156
	8	FfT1	<d.l.	<d.l.	<d.l.	14	12	16
	15	FfT2	<d.l.	36	297	52	20	151
VI	21	GeP	<d.l.	<d.l.	441	145	792	128
	6	GeT1	<d.l.	<d.l.	<d.l.	<d.l.	15	<d.l.
	11	GeT2	<d.l.	85	366	80	287	63
VII	4	ScP	<d.l.	77	961	3,262	2,377	248
	5	SdT	<d.l.	<d.l.	72	21	41	<d.l.
		Average	<d.l.	114	319	408	761	132
		Median	<d.l.	72	258	149	192	117
		Stdev	<d.l.	164	270	798	1,107	106
		Max	<d.l.	591	961	3,262	4,187	343

Table 4: Summary statistics of filter dust phthalate concentrations

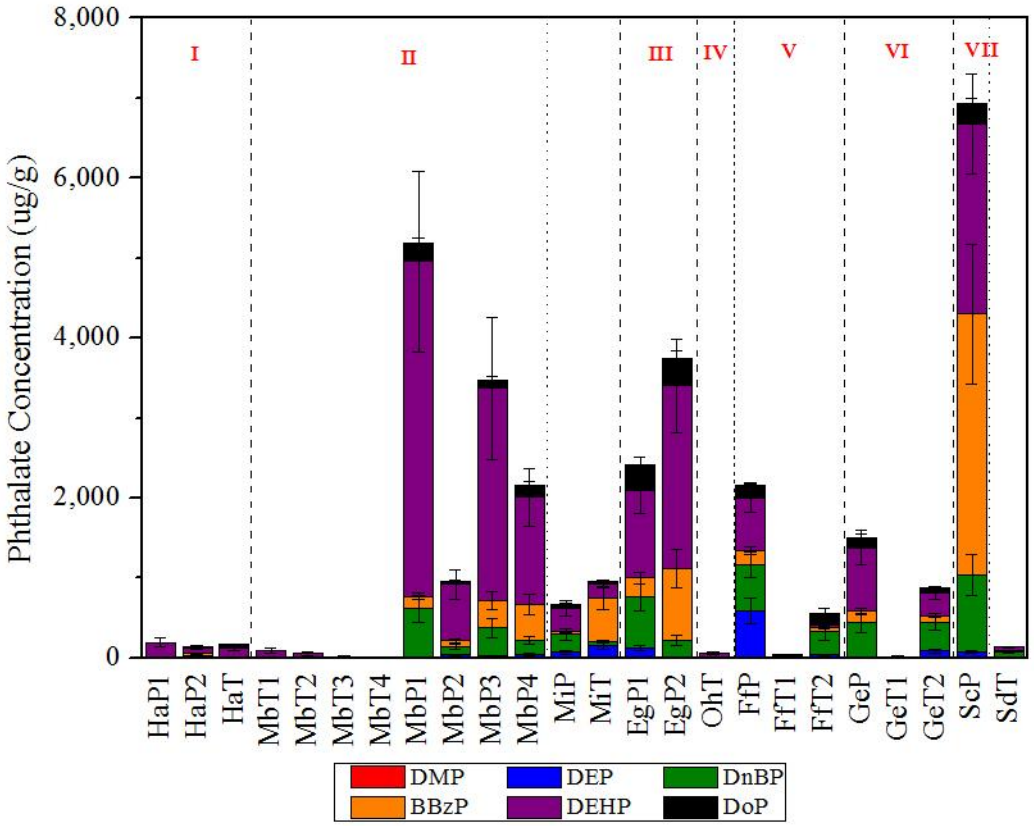

Figure 3: Phthalate filter mass concentration by site.

3.2.2 Polybrominated Flame Retardants

Mass concentrations for fourteen PBDEs were measured from filters collected from recirculating rooftop units. The laboratory analysis is described in more detail in Section 2.3 Table 5 lists the summary statistics for indoor PBDE concentrations in the airborne phase.

Figure 4 contains a bar chart for filter dust mass concentration by site. The bar height represents the average of replicate samples (when available). The uncertainty associated with phthalate measurements is the relative variance between duplicate samples and the overall uncertainty for the analytical procedure explained in Appendix C.

The average (±SD) and median concentration for the sum of the fourteen PBDEs across all sites are 17,850 ± 37,800 ng/g and 6,024 ng/g, respectively. The sites with the highest filter

dust PBDE concentrations are MbP1 (185,690 ng/g) and EgP1 (56,100 µg/g). The sites with the lowest filter dust phthalate concentrations are FfT1 (906 ng/g), and FfP (906 ng/g).

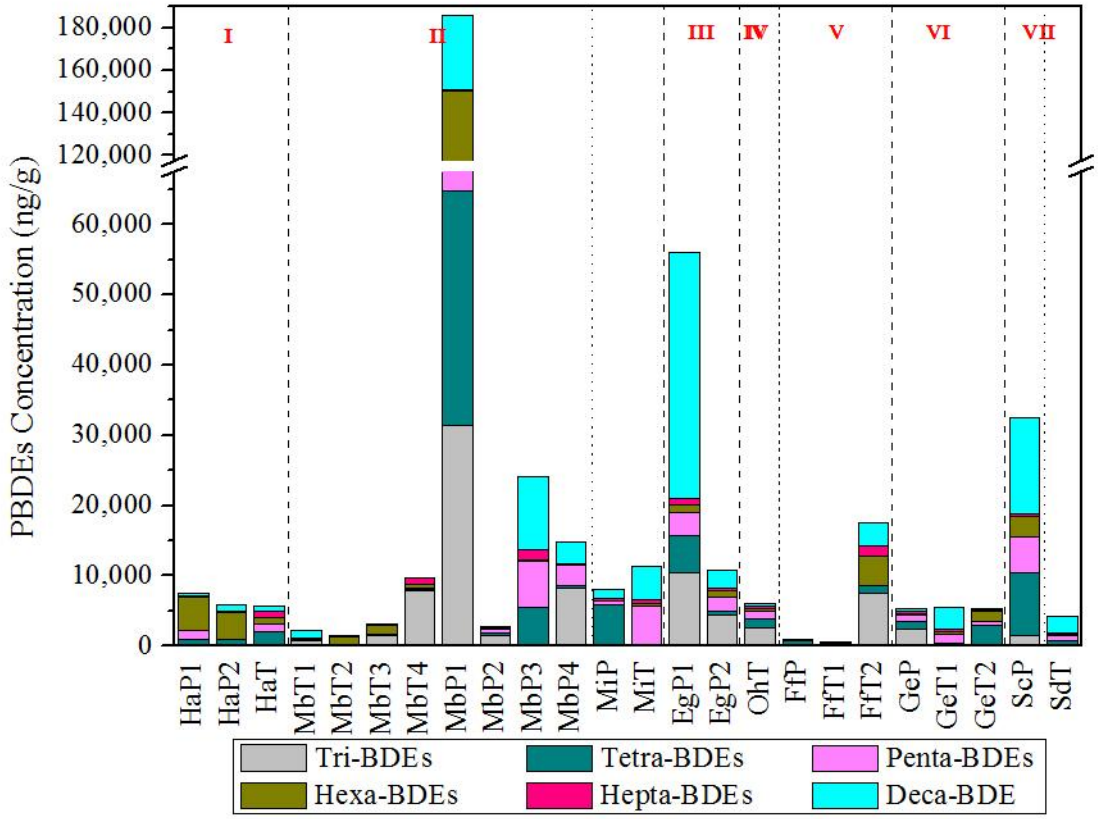

Figure 4: PBDE filter mass concentration by site.

Category Label	Test IDs	Site	Concentration (ng/g)													
			BDE-17	BDE-28	BDE-47	BDE-66	BDE-71	BDE-85	BDE-99	BDE-100	BDE-138	BDE-153	BDE-154	BDE-183	BDE-190	BDE-209
I	1	HaP1	124	79	765	104	--	--	708	522	478	4,050	175	86	150	335
	9	HaP2	4	47	83	767	--	26	74	49	747	3,001	24	115	32	915
	2	HaT	126	123	404	268	1,195	336	638	105	508	202	125	47	819	847
II	3	MbT1	--	787	--	21	10	51	116	38	--	42	24	18	76	1,138
	10	MbT2	--	167	77	79	--	--	--	15	886	120	--	--	72	73
	12	MbT3	--	1,534	--	--	--	--	43	57	1,315	--	--	--	115	147
	19	MbT4	--	7,925	--	205	--	--	--	202	539	26	--	--	782	--
	7	MbP1	395	30,987	--	32,447	930	739	9,259	16,854	57,680	1,197	--	--	715	34,482
	13	MbP2	57	1,458	--	287	100	61	436	--	--	60	47	77	83	170
	17	MbP3	--	--	--	2,982	2,479	5,274	923	375	--	--	182	809	760	10,326
	22	MbP4	8,322	--	316	--	--	--	--	2,840	39	60	--	79	134	3,075
	23	MiP	--	--	--	--	5,884	267	174	208	--	--	--	--	271	1,284
	24	MiT	26	299	--	--	--	2,596	2,555	288	--	303	99	--	394	4,857
III	14	EgP1	--	10,552	--	3,163	2,082	969	1,656	617	--	1,117	--	--	932	35,009
	20	EgP2	1,519	2,951	--	425	167	342	1,422	162	257	696	--	282	119	2,428
IV	18	OhT	53	2,496	--	963	406	167	981	--	--	169	138	191	219	380
V	16	FfP	--	--	280	471	59	9	26	--	14	--	--	--	31	16
	8	FfT1	26	34	68	23	--	--	61	25	85	116	--	--	19	147
	15	FfT2	161	7,285	773	--	397		--	--	1,256	2,943	--	--	1,423	3,377
VI	21	GeP	87	2,280	--	799	359	149	853	--	--	--	111	213	186	282
	6	GeT1	--	258	108	26	--	85	1,179	48	101	43	149	96	250	3,252
	11	GeT2	195	--	1,559	1,234	--	221	309	--	53	1,499	--	17	25	283
VII	4	ScP	1,619	--	6,897	1,927	--	2,725	1,433	1,007	2,692	--	224	103	153	13,799
	5	SdT	--	--	537	264	--	284	399	57	--	37	100	31	114	2,507
		Average	908	4,074	989	2,445	1,172	841	1,162	1,304	4,443	871	116	155	328	5,180
		Median	125	1,458	360	425	401	267	673	182	508	186	118	91	151	1,138
		Stdev	2,200	7,627	1,909	7,327	1,689	1,413	2,018	3,937	14,745	1,237	63	203	372	9,924
		Max	8,322	30,987	6,897	32,447	5,884	5,274	9,259	16,854	57,680	4,050	224	809	1,423	35,009

Table 5: Summary statistics of filter dust PBDE concentrations

Chapter 4: Discussion

4.1 Comparison with Residential Studies

The results detailed in Chapter 3: Results are further discussed in this chapter. These plots show the average concentration found in residential studies done by Rudel et al (2003, 2010), Otake et al. (2001), Adibi et al. (2008), Kanawa et al. (2010), Butt at al (2001), Butte et al. (2001), Kersten and Reich (2003), Becker et al. (2002), Bornehag et al. (2004), Allen et al. 2008, Batterman et al. (2009), Toms et al. (2009), Kanazawa et al. (2010), Schecter et al. (2005), Harrad et al. (2008).

4.1.1 Phthalates

The two most common phthalate congeners found were DEHP (found in all of the airborne phase and filter dust tests) and DEP (found in all airborne phase tests and 14 of the filter dust tests). Plots of the concentration of these two compounds by site are shown in Figure 5 and Figure 6.

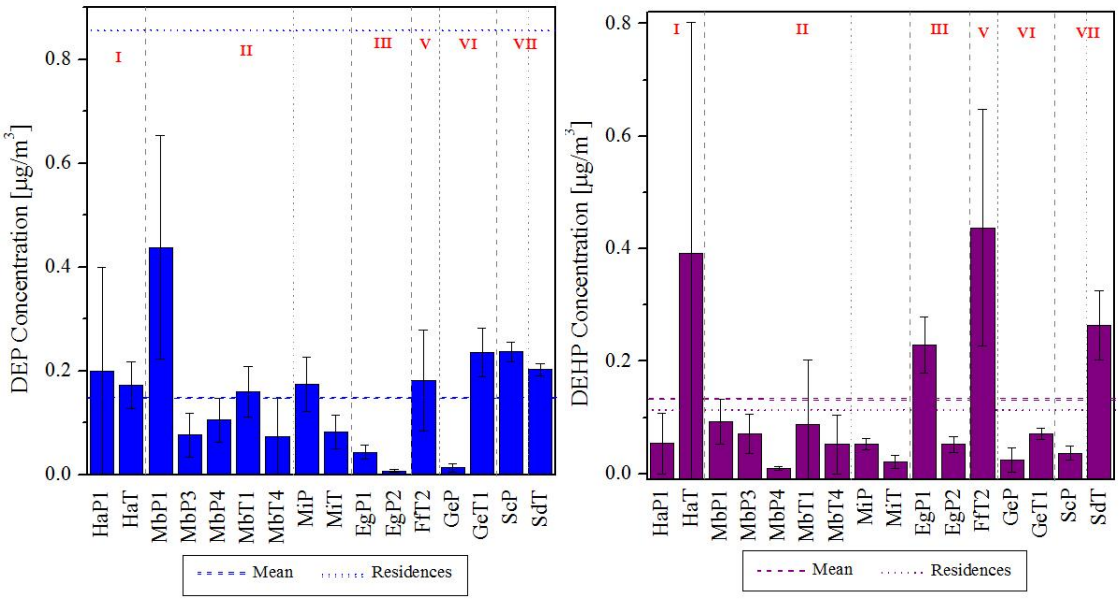

Figure 5: Distribution and comparison of indoor concentration in the airborne phase for DEP and DEHP

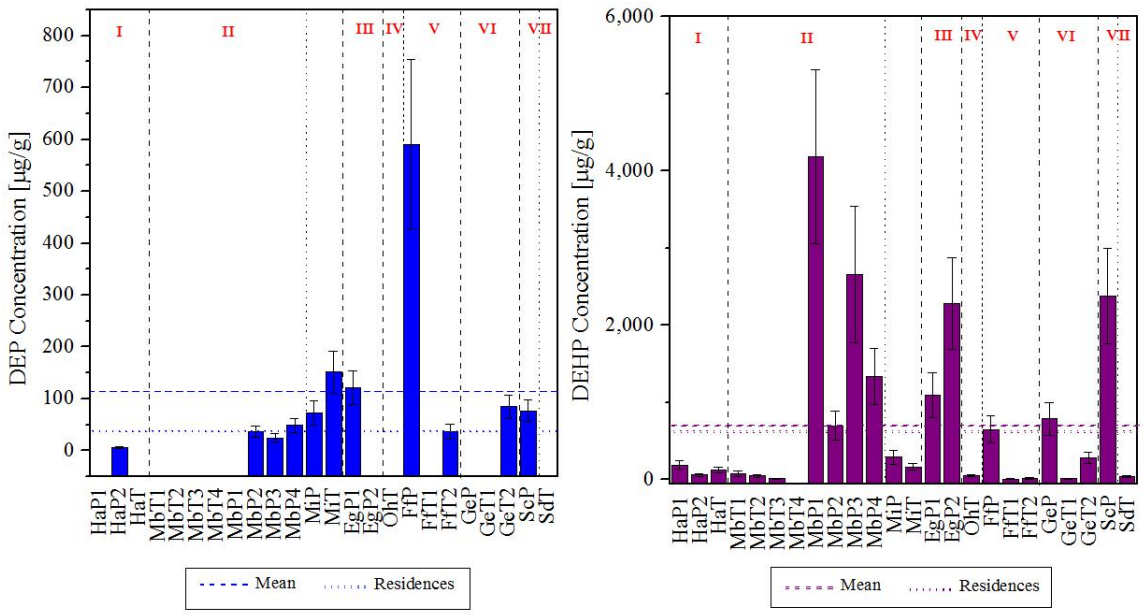

Figure 6: Distribution and comparison of indoor concentration in the filter dust phase for DEP and DEHP

DEP, a plasticizer commonly found in cosmetics and food packaging, was found at higher airborne concentrations in small groceries, test sites ScP and SdT, (average of 0.22 µg/m^3). These small groceries maintain a stock of products packaged for individual consumption compared to larger groceries. The increased surface area of food packaging combined with the smaller interior volume of these stores may have contributed to the higher DEP concentrations observed at these sites. In the dust-phase, DEP was found at higher dust concentrations in a furniture store in Pennsylvania (FfP), and in set general merchandise stores in both Pennsylvania and Texas (MiP and MiT, respectively). DEP is also used in a variety of cosmetics and scented lotions, which is fairly common in this type of stores.

The level of DEP was considerably lower in the airborne phase than the values found in the literature. The average concentration for DEP concentrations in this study was 0.15 ± 0.11 µg/m^3, more than 3 times smaller than the average value of 0.49 µg/m^3 found in seven retail sites in California (Wu et al., 2011), and over 4 times less than the average concentration found in residences found by Rudel et al. (2003, 2010), Otake et al. (2001), and Fromme et al. (2004),

where the average value for all of these houses was 0.67 μg/m^3. One contributing factor to the difference in concentrations might be sampling location within a store, since DEP is one of the most volatile plasticizers we analyzed. For example, we found a higher concentration (0.24 μg/m^3) in a medium sized grocery site in Texas (GeT1), where we sampled next to the cosmetics section of the site. In contrast, in the filter dust phase, the concentration appeared to be much higher when it was detected (Average of 114 μg/g in this study) than in residential studies (47 μg/g)

DEHP, the most widely used phthalate plasicizer plasticizer typically found in level of percent to tens-of-percent level in upholstery, polyvinyl chloride (PVC) flooring, plastics, resins and rubbers (Bornehag et al. 2005), was a plasticizer we found above detection limits in all sites with an average value of 0.12 ± 0.13 μg/m^3 in the airborne phase, and 761 ± 1,100 μg/g in the dust phase. The site with the highest concentration of DEHP was Site FfT2, with an airborne concentration of 0.44 μg/m^3, almost 4 times higher than the average concentration in other sites. This type of store sells a wide variety of home utensils, furniture and other products that could contain high levels of this plasticizer. Home improvement sites also had an increased level of DEHP (0.22 μg/m^3). These sites sell a wide variety of appliances, tools and hardware that are potential sources of phthalates in indoor environments. In the dust phase, DEHP was found primarily in a general merchandise store (MbP) and in an electronics store (EgP), both in Pennsylvania.

DoP is the heaviest phthalate compound we analyzed, and it was only found in 6 out of the 16 Sites in the airborne phase and 16 out of 24 in the filter dust phase. It is a plasticizer with a low vapor pressure that doesn't partition from the solid phase as readily as the other plasticizers analyzed, and it is typically found in wiring, cables and electronics. DoP was found above detection limits in an electronics site in Pennsylvania (GeT), with concentrations of 0.096 μg/m^3 and 0.004 μg/m^3 during the winter and summer, respectively. In the filter dust phase, it was found at a level of 323 μg/g and 343 μg/g during the winter and summer, respectively. Possible sources of this change in concentrations could be different types of electronics and appliances

being introduced during the period of sampling. GeT also had carpet flooring, a surface that SVOCs adsorb strongly to, and continue to emit the compound after the source is removed (Xu et al. 2010). Different ventilation and temperature parameters used in the building during the time of sampling could potentially alter the level at which these compounds desorb from this flooring material.

4.1.2 Polybrominated Diphenyl Ethers

Two PBDEs are selected to be analyzed in greater depth: BDE-47, because it's found at high levels in the blood of US and European residents (Sjödin et al., 2008b), and BDE-209 because it is the only PBDE that hasn't been phased out of manufacture in the US. The concentrations of these two congeners across all retail sites are plotted in Figure 7 and Figure 8.

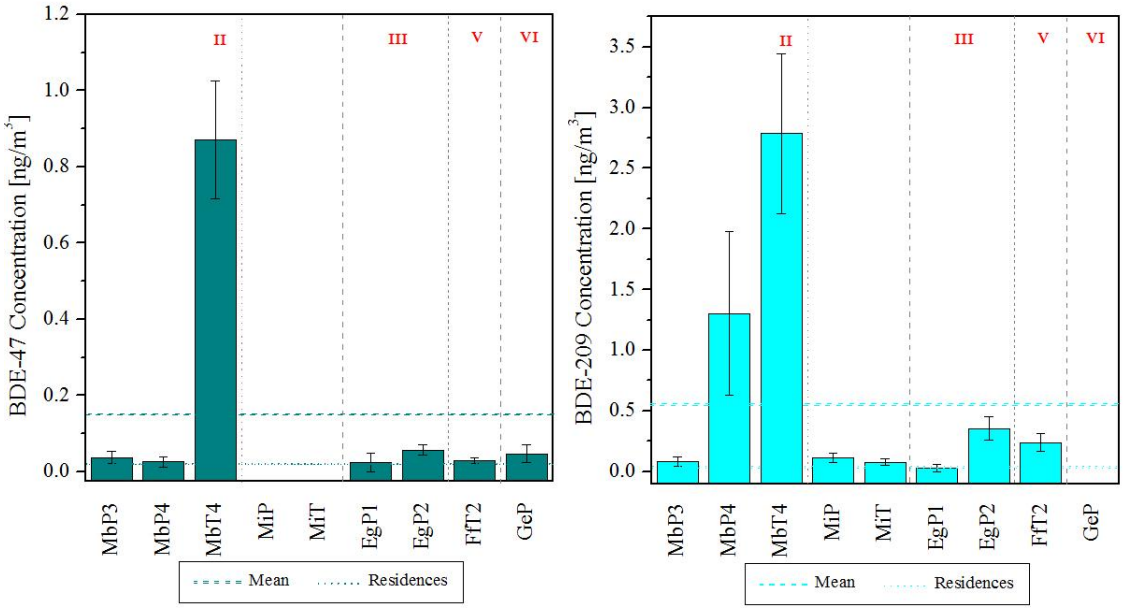

Figure 7: Distribution and comparison of indoor concentration in the airborne phase for BDE-47 and BDE-209.

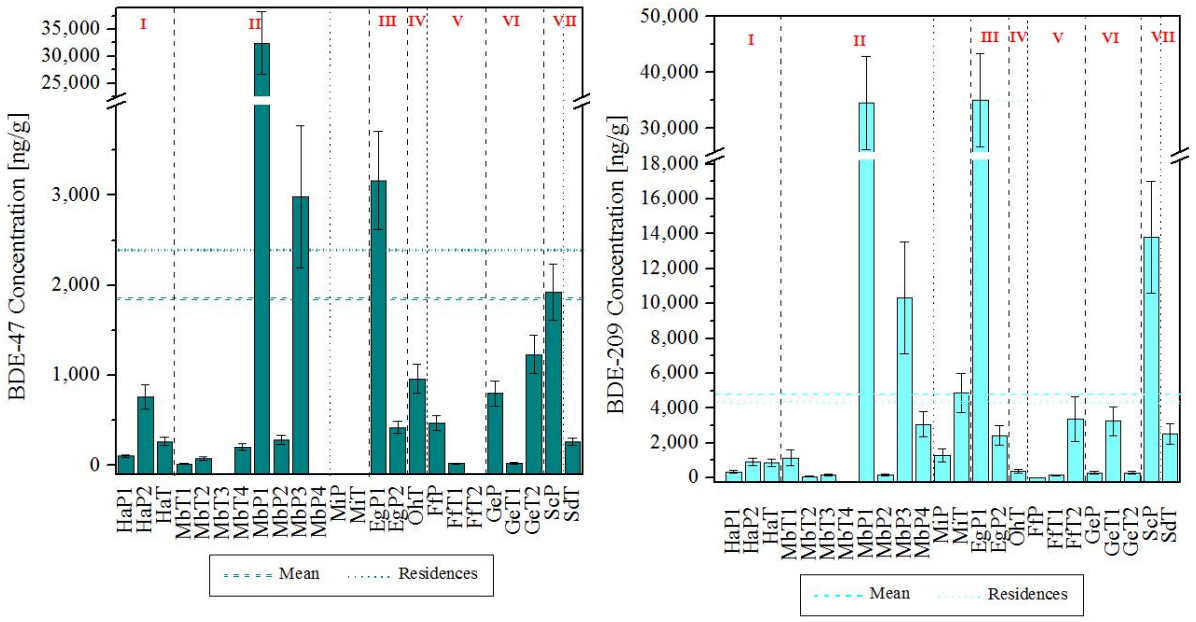

Figure 8: Distribution and comparison of indoor concentration in the filter dust phase for BDE-47 and BDE-209.

BDE-47 is a penta-BDE normally used as a flame retardant in polyurethane foam products (furniture, mattresses and carpet padding), and it was also one of the many flame retardants phased out of U.S. manufacture in recent years (USEPA, 2006). In the airborne phase, it is found at high levels in blood and breast milk in the general population (Toms et al., 2008), and we found it at concentrations similar to residential levels (0.02 ng/m^3). The only exception was Site MbT4, with an elevated concentration of 0.87 ng/m^3. In the filter dust phase, it was found in 19 Sites, at levels below what is typically found in residential levels. There are three possible explanations for the persistent levels of this congener. The first one is debromination, a process by which heavier PBDE (such as decabromo diphenyl ether, BDE-209) congeners occurring indoors degrade into lower brominated congeners (Eriksson et al., 2004). Another reason is the presence of building materials that adsorb SVOCs and might reemit them long after the source has been removed. A third mechanism is the contribution of products manufactured abroad which might still use these PBDEs as a flame retardant in these products.

BDE-209, a fully brominated-BDE is the only brominated flame retardant that hasn't been phased out from manufacturing in the United States. It is used as a flame retardant in high impact polystyrene (HIPS) television set cabinet backs and commercial upholstery fabric. By mass, this was the compound found at higher levels than any other PBDE throughout most sites. The average concentration for BDE-209 was 0.64 ± 0.91 ng/m^3, considerably higher than the concentration reported in residential settings by Fromme et al (2009, 0.03 ng/m^3). Airborne concentrations of BDE-209 were higher in general merchandise sites, especially for MbP4 (1.30 ng/m^3) and MbT4 (2.79 ng/m^3). Filter dust concentrations were higher in general merchandise and electronic sites, especially for EgP1 (35,000 ng/g) and MbP1 (34,000 ng/g).

4.2 INTER-PHASE RELATIONSHIPS

A statistical analysis was performed to attempt to determine a relationship between filter dust and airborne concentrations. The summary of the findings is shown in Table 6. The linear regressions of the data do not establish a significant relationship for the majority of these compounds. One of the biggest factors that influenced this is the limited amount of data, with DEHP (shown in Figure 9) being the compound with more than 10 coupled counts. An outlier analysis was not conducted due to the limited size of the dataset.

SVOC	n	Intercept (*/m^3)	Slope (g/m^3)	Adj. R^2	<p-value
DMP	NA		NA	NA	NA
DEP	7	2.49E-01	-1.40E-03	0.19	0.18
DBP	8	9.50E-02	-7.89E-05	0.25	0.12
BBzP	8	2.21E-02	1.90E-05	0.02	0.33
DEHP	13	4.20E-02	-1.65E-05	0.07	0.19
DoP	5	6.37E-03	-2.88E-05	-0.31	0.84
BDE-17	4	7.62E-02	-4.12E-07	-0.50	0.96
BDE-28	6	6.87E-01	-8.10E-05	0.48	0.08
BDE-71	2	-6.01E-01	2.14E-03	--	--
BDE-66	4	2.51E-01	-5.81E-05	0.43	0.21
BDE-47	5	3.86E-02	-3.22E-06	-0.27	0.73
BDE-100	6	2.39E-02	6.25E-06	-0.13	0.56
BDE-99	4	1.19E-01	2.36E-05	0.03	0.16
BDE-85	5	1.82E-01	-2.84E-04	0.12	0.30
BDE-154	4	-2.66E-03	1.99E-04	0.50	0.18
BDE-153	5	5.05E-02	-1.16E-05	-0.12	0.51
BDE-138	3	-4.78E-03	1.86E-04	0.93	0.12
BDE-183	3	2.92E-02	-2.65E-05	0.56	0.31
BDE-190	8	3.66E-02	-2.98E-05	0.19	0.16
BDE-209	7	1.83E-01	-4.48E-06	0.41	0.07

*** - µg for phthalates, ng for PBDEs.**

Table 6: Summary of air-dust correlation of SVOC samples

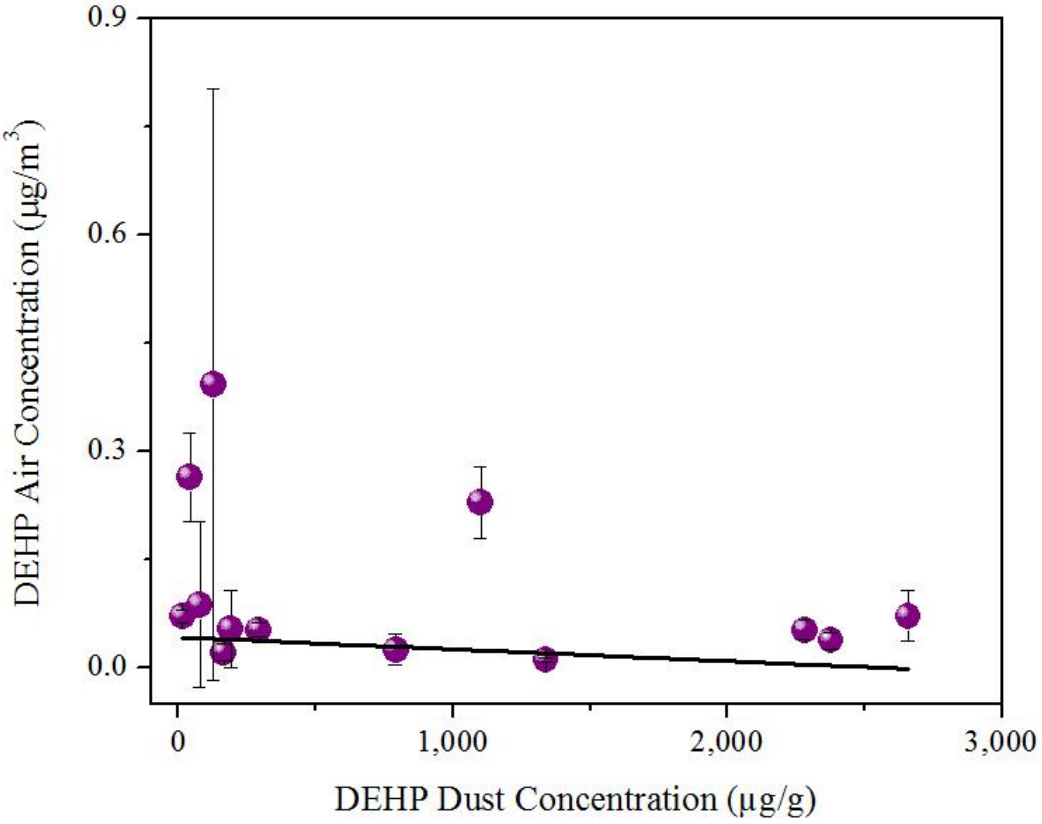

Figure 9: DEHP air-dust curve

It is important to note that airborne concentrations should not be taken as purely gas-phase concentrations. The air samples were measured in such a manner that does not prevent from particles to load into the sorbent/PUF tubes; particle-phase concentrations contribute to an unknown fraction of the airborne concentrations. Additionally, some of the air handling units from which the filters were collected had their outdoor air damper opened; as a result, the filter samples included particles collected from outdoor air in addition to the particles collected from recirculated indoor air. Lastly, airborne concentrations reported in this study were measured over a 48-hour period which may not accurately reflect the average concentrations over the 30 days needed for the dust sampling.

4.3 VENTILATION RELATIONSHIPS

Airborne SVOC concentrations were not correlated with measured ventilation rates. Air exchange rates reported in this study were measured over a 4-hour period which may not accurately reflect the average air exchange rate over the 48 hours needed for the SVOC sampling. For the intervention site, we measured SVOC concentrations using both normal and elevated air exchange rates at Site MiT. Both measurements were placed in the same location during each sampling event.

4.3.1 Phthalates

Figure 10 shows the plot of phthalate concentrations categorized versus air exchange rates. It should be noted that the air exchange rates reported in this study were measured over a 4-hour period and may not reflect the average ventilation rate for the 48 hour sample time needed for SVOC sample collection.

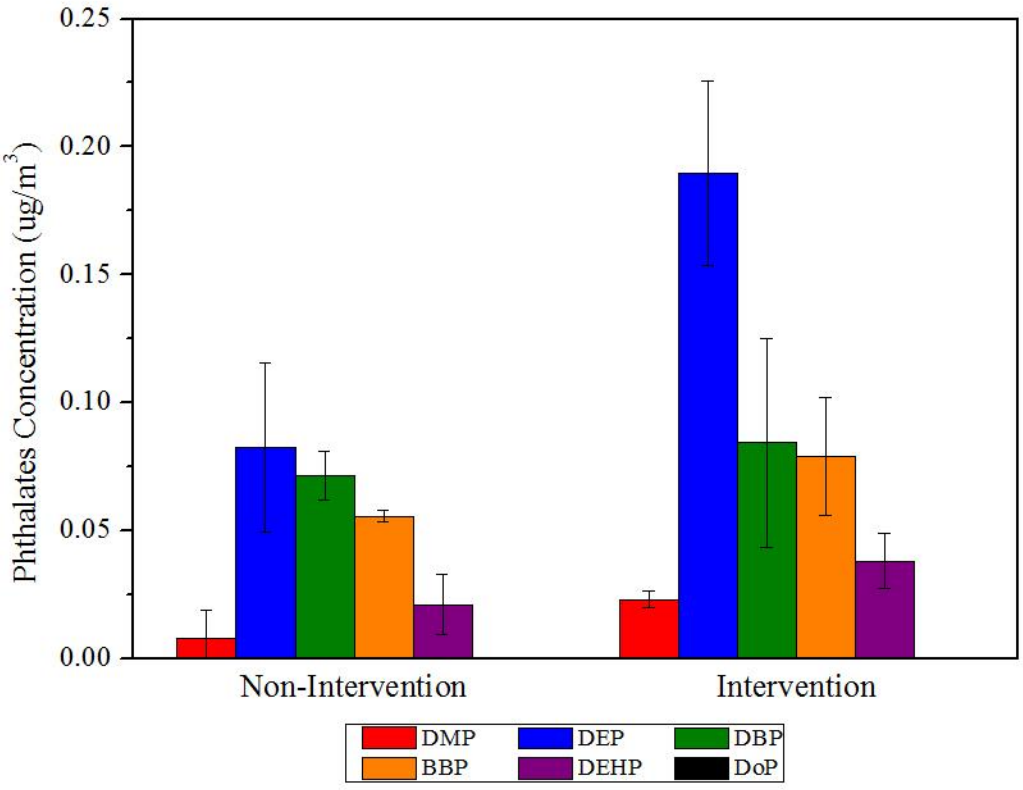

Figure 10: Phthalate indoor concentration by air exchange rate for MiT site.

All phthalates (except DoP) were found above detection limit in both tests. The concentration of all of the phthalates increased with the increased ventilation. Possible contributions to these increased phthalate levels may be attributed to increases in the indoor temperature observed for the higher ventilation rate.

It is important to note that the uncertainty of this sum is quite large, and no significant conclusion can be made about the fate and transport of these phthalates as a function of air exchange rate. Another factor that could influence the variability of these compounds includes different sources being added or removed during the time of sampling. Lastly, increased temperatures are a possible contributing factor to the increased concentration of the more volatile phthalates.

4.3.2 Polybrominated Dyphenil Ethers

Similarly to phthalates, airborne PBDE concentrations were not correlated with reported ventilation rates, except for the intervention site. Figure 11 shows PBDE concentrations categorized by air exchange rate.

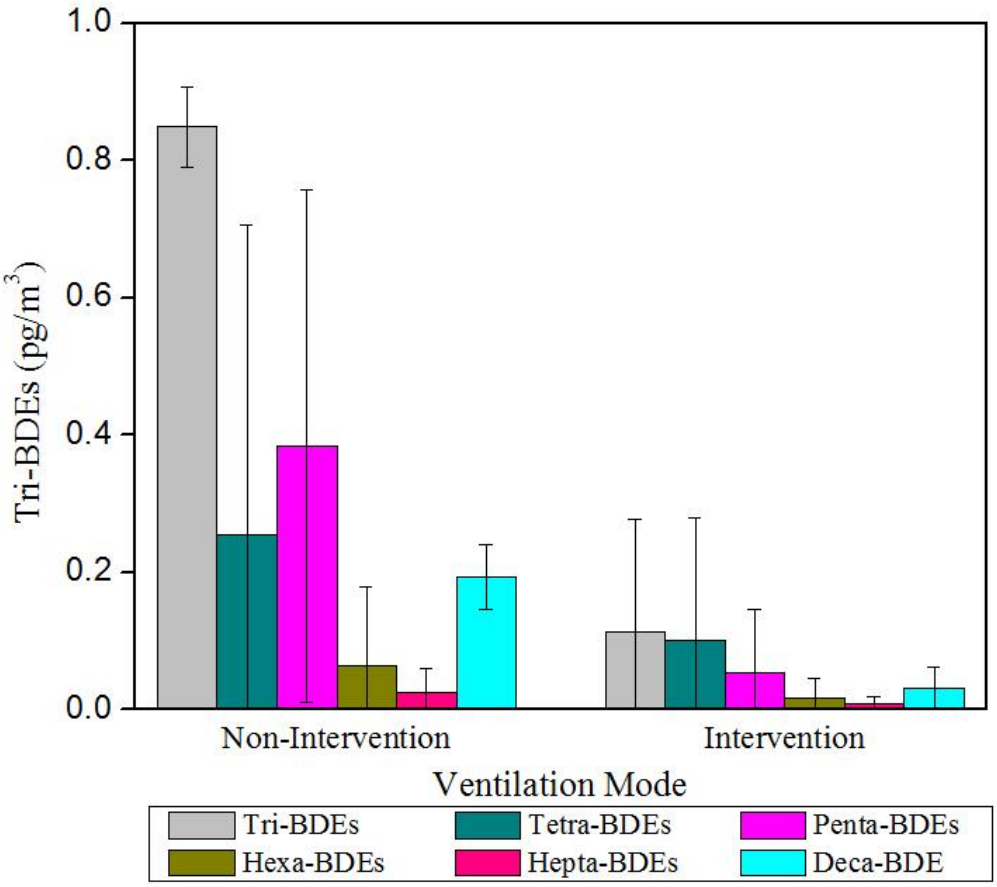

Figure 11: PBDE indoor concentration by air exchange rate for MiT site.

All of the PBDE groups saw a drop in concentration followed by the increased ventilation rate. These results show a much bigger difference for PBDE concentrations and higher ventilation rates. It is theoretically expected that increasing the ventilation rate would decrease PBDE indoor concentrations, since it could potentially decrease the levels of particles and dust, to which PBDEs strongly adsorb to. It is important to note that the uncertainty of this assessment is quite large, and it is difficult to make a definitive statement about the fate and transport of these compounds. Other factors that could influence the variability of these compounds include different sources being added or removed between periods of sampling.

4.4 TEMPERATURE

All statistical analysis was performed to attempt to determine a relationship between airborne SVOC concentrations and indoor temperatures. Temperature measurements were recorded every 5 minutes in five locations for each site. The average temperatures of the five sensors in the middle level during the SVOC sampling was correlated with phthalate and PBDE concentrations. The summary statistics of the correlation are shown in Table 7.

SVOC	n	Intercept (˚C)	Slope (˚C/*)	Adj. R^2	>p-value
DMP	10	-0.359	-0.021	-0.102	0.699
DEP	15	-0.044	0.011	-0.001	0.341
DBP	14	1.221	-0.044	-0.030	0.446
BBzP	10	0.377	-0.014	0.243	0.084
DEHP	15	-0.244	0.016	-0.028	0.448
DoP	6	0.726	-0.031	0.732	0.019
BDE-17	8	-0.189	0.012	0.036	0.597
BDE-28	9	0.310	-0.010	0.059	0.772
BDE-71	6	0.255	0.001	0.063	0.565
BDE-66	8	-0.194	0.011	0.048	0.447
BDE-47	7	-0.002	0.002	0.045	0.896
BDE-100	8	0.002	0.001	0.011	0.837
BDE-99	9	-0.647	0.035	0.009	0.487
BDE-85	7	-0.430	0.022	0.066	0.446
BDE-154	8	0.056	-0.002	0.076	0.676
BDE-153	8	-0.055	0.005	0.095	0.560
BDE-138	8	0.070	-0.003	0.059	0.429
BDE-183	7	-0.024	0.002	0.045	0.542
BDE-190	8	-0.042	0.003	0.056	0.721
BDE-209	8	-0.040	0.008	0.111	0.820

*** - µg for phthalates, ng for PBDEs.**

Table 7: Summary of indoor air-temperature correlation of SVOC samples

The only SVOC that showed a moderate relationship (R^2 = 0.732) with indoor temperature was DoP. BBzP was the second compound with the highest relationship (R^2 = 0.2426), but significantly lower than the one for DoP. PBDEs did not exhibit a strong

relationship with temperature. A reason for this is that there is insufficient data for PBDEs in the airborne phase to draw any conclusive evidence of this behavior. Additionally, eliminating outliers under any statistical analysis with such a small amount of data ($n \leq 15$) is not recommended.

Chapter 5: Conclusions

The main finding of this field research work is the characterization of different concentrations of phthalates and polybrominated diphenyl ethers (PBDES) in retail stores, as well as establishing links with observed building use parameters that could have a potential effect on the source and fate of these compounds. In general, the SVOC concentrations monitored in the present investigation seemed to be consistent with levels previously reported in residential environments. The inter-phase relationship between the airborne and the field dust concentrations could have a possible effect on the exposure to these compounds as related to particle and dust levels in the retail environment. There are no exposure limits set for these compounds, so a human risk assessment for employers and customers is not possible with the present information. Phthalates and PBDEs are source-driven, since these are man-made chemicals not found outdoors and used to improve physical properties of consumer products. The existence and concentrations of these compounds depends primarily on the type of consumer products used, and they can persist in built environments long after the source is removed due to external adsorptive sinks, such as particles, carpets, floor and settled dust. Several confounding building parameters could alter the concentration of SVOCs in these environments, such as temperature, air exchange rate and relative humidity.

Appendix A: Protocol for Measuring Ambient SVOC Concentrations Using Adsorbent Cartridges and Pumps

Purpose: We will look at a group of 10 SVOCs, 5 plasticizers and 5 brominated flame-retardants. These measurements will provide time-integrated measurements. For the pilot study we will use Tenax tubes as well as PUF (polyurethane foam) tubes.

Background: In this project, we will focus on a subgroup of SVOCs that are used as additives that are often present at high levels in indoor products (10-30% by mass), worldwide production for SVOCS used as additives is extremely large, many of these SVOCs have adverse health effects, and association of plasticizer and flame retardants in indoor air with building characteristics has not been studied before. SVOC additives are also likely ubiquitous in all types of retail environments and this is the class of compounds that Hartmann et al. (2004) chose to explore.

Certainty: Certainty will depend of the handling of the samples as well as field blanks, spikes, and calibration curves of the GC-MS.

Measurement Procedure: Prior to collecting a sample, the volumetric flow rate through the sample pump must be calibrated.

Note: People and their personal care products are a common source of contamination when collecting field data. Try to minimize the use of these products when collecting field samples. Always wear nitrile gloves when handling the field sampling equipment.

Pump Calibration Procedure:

1) Place two Tenax tubes together by using two ¼" ID Stainless Steel Swagelok unions with PTFE ferrules. Make sure that the direction of the sampling flow arrows is the same (see Figure 12).

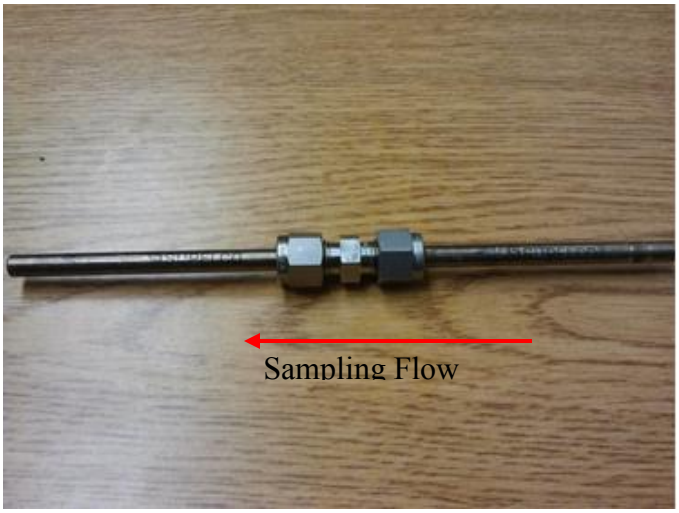

Figure 12: Assembly of Tenax Tubes' System

2) Attach the sample pump to the outlet of the calibrating device. Turn on the calibrator and allow it to complete its diagnostic check (Check Figure 13). Note: If calibrator does not come on or bubbles do not form, check the calibrator manual for trouble shooting instructions.

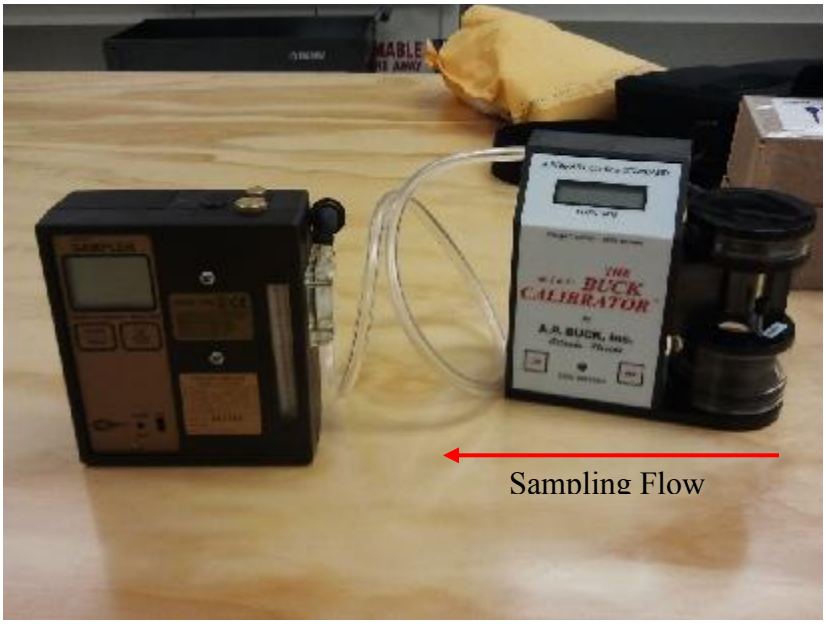

Figure 13: Arrangement of Calibration System

3) Turn on the Airchek sample pump by moving the small square button up to "ON".
4) If there is no flow, press the "START/HOLD" button. If there still is no flow, check the pump manual for troubleshooting instructions.
5) To reset the sampling period number shown in the pump, turn off the device by moving down the button from the "ON" position, then turn pump on again.

6) If the flow rate is within 400±40 cc/min no adjustment to the flow rate is needed. If the flow rate is outside of 400±40 cc/min, the flow rate must be adjusted.
7) Three small screws can adjust the flow rate. To increase the flow rate, turn the screw to the left. Conversely to decrease the flow rate turn the screw to the right. Care should be used when adjusting the screw small changes can dramatically affect the flow rate, and it is also possible to inadvertently remove the screws from their fitting. The first one is located in the next to the "ON" switch for minor flow adjustments; a second one is located on the tubing connecting the calibrator to the pump for larger adjustments. If the flow is still considerably different, a third screw can be located in the top part of the sample for major adjustments (see figure 14 for reference).

Figure 14: Sampling Air Pump and Flow Adjustment Screws

8) Once the desired flow rate has been achieved, disconnect the calibration device from the sampling pump.
9) Attach the representative sorbent tubes to the inlet of the air sampling device using flexible tubing outfitted with an insert of ¼" ID Teflon® tubing. Be sure that the sampling flow arrows of the sorbent tube are directed towards the air sampling pump.
10) Attach the other end of the sorbent tubes to the outlet of the calibrating device using flexible tubing outfitted with an insert of ¼" ID Teflon® tubing. Be sure that the sampling flow arrows of the sorbent tube are directed away from the calibrating device.
11) If the flow rate is within 80±5 cc/min no adjustment to the flow rate is needed. If the flow rate is outside of 80±5 cc/min, the flow rate must be adjusted (repeat step 7 to achieve desired flow rate).
12) Once the desired flow rate has been achieved, measure the flow rate three times and record the flow rate measurements and their average on the Sorbent Tube Field Data Sheet.
13) Once the flow rate has been recorded, turn off the air-sampling pump by switching the power button down.

Sample Collection Procedure:

1) Tubes must be conditioned for at least 30 min and checked in the MS to be blanked out. They should be then sealed immediately with the appropriate fittings, wrapped in clean aluminum foil and put in a clean, airtight, opaque container and stored at < 4C.
2) At the sample location, let tubes come to ambient temperature.
3) WITH GLOVES take caps off tubes, connecting primary and back-up tubes with couplings, and attach to pump with non-off gassing hose.
4) Uncap and immediately reseal field blanks and place them back into the storage container.
5) Turn pump on, note flow rate time, temperature, air pressure, and RH.
6) Run pump at 75-85 ml/min for 48 hours.
7) Disconnect bubble generator after the pump has flow has been stabilized.
8) At end of sampling period, note flow rate, time, temperature, air pressure, and RH.
9) Immediately remove tubes, cap, and place in aluminum foil, place in container mentioned above.
10) If shipping, or time until analysis to be longer than 1 day, refrigerate at < 4C.

Field Audit Procedure:

1) After collecting a sample, it is necessary to confirm the flow rate of the pump and sample tube combination. To confirm the flow rate, attach the actual sample tube to the outlet of the calibrator using the flexible tubing outfitted with an insert of ¼ inch ID Teflon tubing. Be sure that the large end of the sorbent tube is attached to the Gilibrator-2.
2) Attach the sample pump to the outlet of the Bubble Generator.
3) Quickly measure the flow rate and record it on the field data sheet. If the audit flow rate varies outside the range of 20±3 cc/min, the sample may be invalidated. If the sample flow rate is outside the range of 20±3 cc/min, turn off the pump by pressing "ON/Hold" key and consult with the field site manager/coordinator before proceeding.
4) After stopping the pump, record the flow rate on the field sample data sheet.
5) Remove the sorbent tube from the Gilibrator and put it into its stainless steel sheath. Check the number of the metal sheath with the number recorded on the field data sheet. Sign the Field Data sheet.
6) Fill in the information required on the Sorbent Tube Chain of Custody Form.
7) Wrap the sample sheath with aluminum foil, put the wrapped sheath into a plastic "zip lock" bag and put the bag into the cool storage chest. Note: Sorbent tubes should be stored at 4°C or less to prevent degradation.

Trip and Field Blanks: A trip blank and a field blank must be "collected" for each test site. The procedure for collecting these blanks is given below:

Trip Blank:

1) Prior to leaving for a test site, remove 1 sample tube from the cooler and record their ID number, date and time on a Sorbent Tube Field Data Sheet. Gloves should always be worn when handling sorbent tube sheaths or sorbent tubes.

2) Briefly remove the sorbent tubes cap and then put it back on. Record the sorbent types and write "Trip Blank" on the Sorbent Tube Field Data Sheet. Sign the field data sheet.
3) Enter the information for the Trip Blanks on the Sorbent Tube Chain of Custody form.
4) Wrap the sample sheaths with aluminum foil, put the wrapped sheath into a plastic "zip lock" bag and put the bag into the cool storage chest.

Field Blank:

1) While at the test site and actively collecting samples using sorbent tubes, remove 1 sample sheaths from the cooler and record the sheath ID numbers, the date and time on a Sorbent Tube Field Data Sheet. Gloves should always be worn when handling sorbent tube sheaths, or sorbent tubes.
2) Briefly remove the sorbent tubes from their sheath and then return it to the sample sheath. Record the sorbent types and write "Field Blank" on the field data sheet and sign the Field Data Sheet.
3) Enter the information for the Field Blanks on the Sorbent Tube Chain of Custody form.
4) Write the sheaths number on the "zip lock" plastic bag. Wrap the sample sheaths with aluminum foil, put the wrapped sheaths into the labeled plastic bag and put the bag into the cool storage chest.

Shipping and Handling: The US EPA protocol for sorbent tubes requires field samples be stored wrapped in aluminum foil at a temperature of less than 4°C. To keep the sorbent tubes cool, place sorbent tubes into their sheaths, wrap the sheath with aluminum foil, put the wrapped sheath into a plastic "zip lock" bag and put the plastic bag in a cooler kept cold with "blue" ice. DO NOT use ice to keep the tubes cool. The liquid water that forms as the ice melts can contaminate the sorbent tubes.

Before the samples are sent to the laboratory check the information on the Sorbent Tube Chain of Custody Form. If the information is correct, sign and date the Relinquished by line on the bottom of the form. Be sure the chain of custody form is shipped with the samples.

When the samples are packed to send to the laboratory for analysis, be sure to put completely frozen blue ice packets in the cooler. Use packing material to prevent the samples from moving in the cooler and ship the cooler using next day air with delivery before 10:00 AM to:

Ying Xu
The University of Texas at Austin
10100 Burnet Rd.
Center for Energy and Environmental Resources Bldg., #133
Austin, TX 78758

FIELD DATA SHEET (FDS)

GENERAL INFORMATION

SITE CODE:_____ DATE(S) SAMPLED:_____

TIME PERIOD SAMPLED:_____

LOCATION SAMPLED:_____ OPERATOR:_____

PUMP NUMBER:_____ CALIBRATED BY:_____

PUMP CALIBRATION DATA

TARGET FLOW RATE	CC/MIN
MEASUREMENT 1	CC/MIN
MEASUREMENT 2	CC/MIN
MEASUREMENT 3	CC/MIN
AVERAGE FLOW RATE	CC/MIN

ADSORBENT CARTRIDGE INFORMATION

ADSORBENT:_____ SAMPLE SERIAL NO#1:_____
SAMPLE SERIAL NO#2:_____

SAMPLING DATA

AMBIENT TEMP (∞F)	AMBIENT PRESS (IN. HG)	FLOW RATE (CC/MIN)	SAMPLING PERIOD START	STOP	TOTAL SAMPLING TIME (MIN)	TOTAL SAMPLING VOLUME (CC)

FIELD AUDIT

INITIAL FLOW RATE :_____CC/MIN
AUDIT FLOW RATE:_____CC/MIN
Audit Flow Check Within 10% of Set Point (Y/N)?

CHECKED BY:_____

DATE:_____

Sorbent Tube Chain of Custody Form

Site ID:_____

Tube ID Number	Date Sampled	Time Sampled	Air Volume (L)

Collected by:	Date:
Relinquished by:	Date:
Analyzed by:	Date:

Appendix B: Protocol for Sampling Ambient sVOC Concentrations via PUF extraction

PUF EXTRACTION

Apparatus

- Sonication system manufactured by Branson 3510
- Volumetric glass flasks
- Nitrile examination gloves from Microflex
- Aluminum foil
- Ice substitute bags manufactured by Coleman
- Rotary Evaporator system manufactured by IKA RV-10
- 10 ml glass pipette
- Syringeless filter device with 0.45µm PTFE membrane and glass microfiber prefilter and polypropylene housing manufactured by Whatman
- Autovial plunger with ears manufactured by Whatman
- Custom-made glass flask (1.5" D × 5" L)
- Amber glass flasks manufactured by National Scientific
- Flask caps with septa
- Vial insert, 250 µl glass with polymer feet manufactured by Agilent
- Nitrogen cylinder (UHP)
- Analytical balance manufactured by Citizen

Chemicals

- 7X Cleaning Solution, MP Bio
- Methanol, assay 99.8%, VWR chemicals
- Hexane, assay ≥99%, Sigma-Aldrich chemicals

Glassware clean-up

All glassware was washed with hot water and cleaning solution and rinsed two times with water from the tap. Then, ultrapure water was used to rinse the glassware, followed by rinsing with methanol. Hexane was then used to rinse all the glassware to remove contaminates. All glassware was dried in a 100°C oven for one hour and stored in a clean environment to prevent accumulation of dust and contamination.

Initial amber flask weighing

A vial insert placed inside an amber glass flask and covered with a cap is weighed three times to a precision of 0.01 mg. Each weight is recorded, and an average value is used to determine the weight of the empty flask with cap.

Sonication

After sampling, the PUF cartridge was returned to its original container and safely stored in a refrigerator at a temperature of ≤4°C. The PUF cartridge was taken to the laboratory and placed in a 150ml volumetric glass flask. The PUF Cartridge was sonicated with 100 ml of hexane for 45 minutes, and then poured into a 1 liter rotary evaporator glass flask. An ice substitute bag was placed inside the sonicator next to the flask, and aluminum foil was used to cover the flask, to prevent evaporation of the samples. This procedure was repeated 2 additional times.

Rotary evaporation

The rotary evaporator glass flask was then connected to the rotary evaporation apparatus. The flask was then lowered to a bath of water heated up to 80°C and rotated at a rate of 30 Hz. Rotary evaporation was done until the final 5 ml concentrate were collected in the bottom of the flask.

A syringeless filter device was placed on top of the custom-made glass flask. The concentrate was lightly stirred while still in the 1 liter glass flask to collect any chemicals that

might have sorpted to the inner surface of the flask. The concentrate was then transferred using a 10 ml glass pipette to the syringeless filter device.

5 ml of hexane were then poured into the 1 l glass flask, and rotated at a rate of 100 Hz to collect any left-over residuals that might have sorpted to the glass. Then, the hexane is transferred to the syringeless filter device. This procedure was then repeated 3 times.

The concentrate is then pushed from the filter device into the tall glass flask with an autovial plunger with ears. The plunger is removed, and 10 ml are poured into the filter device to collect any chemicals that might have sorpted to the inner surface of the filter device.

Nitrogen blow down

The extract is then placed in an inert atmosphere (such as a fume hood). A nitrogen blow needle is then lowered and submerged into the concentrate. The nitrogen should be very clean, and adjusted to provide a gentle stream. Nitrogen blow down was done until the final 150 µl was collected into the bottom of the flask. NOTE: This process can take several hours.

The concentrate is then transferred to the empty weighed amber flask using a 100 µl syringe. 60 µl of hexane are poured into the custom-made flask to collect any chemicals that might have sorpted to the inner surface of the flask. Then the hexane is transferred to the amber flask. This procedure is done twice.

Volume determination

The amber flask with the concentrate is then weighed again 3 additional times. Using the density of the hexane (in this case 0.672 g/ml), the exact final volume of the concentrate inside the flask is calculated.

Analysis

Phthalates

A GC-FID (Agilent 7890A) system was operated using a 4:1 split injection. The inlet temperature was set at 275°C and a constant column flow was set at 1.2 ml/min. The oven

temperatures were programmed from 120°C for 2 min, ramp 12°C/min for 15 min, hold 3 min, then ramp 20°C/min for min, hold 2 min. The detector was set at 320°C.

Polybrominated Diphenyl Ethers

A GC-μECD (Agilent 7890A) system was operated using a pulsed splitless injection with an injection pulse pressure at 30 psi until 1 minute and a purge flow to split vent of 50 mL/min at 1.5 min. The inlet temperature was set at 325°C and a constant column flow was set at 1.1978 ml/min. The oven temperatures were programmed from 80°C for 0.5 min then ramp 20°C/min for 13.5 min, hold 2 min. The detector was set at 360°C.3

Appendix C: Quality Assistance/Quality Control

CALIBRATION

6 phthalates are being analyzed in this study, which include:

- Diethyl Phthalate (DEP),
- Dimethyl Phthalate (DMP),
- Di-n-butyl Phthalate (DBP),
- Butyl Benzyl Phthalate (BBP),
- Di(2-ethylhexyl) Phthalate (DEHP),
- Di-n-octyl Phthalate (DoP)

5 different liquid concentrations were prepared per each compound, with the following values (µg/µl): 0.01, 0.02, 0.05, 0.1 and 0.2. Each concentration was injected 3 times into a GC-FID, which gives a response in units of Pico Amperes (pA), and then the values were averaged out. Table 8 shows the current calibration values for the phthalates. Each calibration point showed a small coefficient of variance (≤4%), and the correlation coefficients from signal response to injected amount show a strong relationship (R2 ≥ 0.995) from the standards prepared.

Phthalate	Slope (µg/pA)	R^2
DEP	682.08	0.9949
DMP	768.76	0.9973
DBP	894.38	0.9979
BBP	952.57	0.9976
DEHP	1046.41	0.9995
DoP	1015.62	0.9993

Table 8: Calibration of phthalates with slope and correlation coefficient

14 polybrominated diphenyl ethers (PBDEs) are being analyzed in this study, which include:

- 2,2',4,-Tribromodiphenyl ether (BDE-17),
- 2,4,4'-Tribromodiphenyl ether (BDE-28),
- 2,2',4,4'-Tetrabromodiphenyl ether (BDE-47),
- 2,3',4,4'-Tetrabromodiphenyl ether (BDE-66),
- 2,3',4',6-Tetrabromodiphenyl ether (BDE-71),
- 2,2',3,4,4'-Pentabromodiphenyl ether (BDE-85),
- 2,2',4,4',5-Pentabromodiphenyl ether (BDE-99),
- 2,2',4,4',6-Pentabromodiphenyl ether (BDE-100),
- 2,2',3,4,4',5'-Hexabromodiphenyl ether (BDE-138),
- 2,2',4,4',5,5'-Hexabromodiphenyl ether (BDE-153),
- 2,2',4,4',5,6'-Hexabromodiphenyl ether (BDE-154),
- 2,2',3,4,4',5',6-Heptabromodiphenyl ether (BDE-183),
- 2,3,3',4,4',5,6-Heptabromodiphenyl ether (BDE-190),
- Decabromodiphenyl ether (BDE-209)

7 different liquid concentrations were prepared per each compound. For the first 13 PBDEs, the following concentrations were prepared (ng/µl): 0.025, 0.05, 0.1, 0.25, 0.5, 1 and 2. For BDE-209 only 4 concentrations were detected, which were (ng/µl): 2.462, 4.924, 9.848 and 24.62. Additionally, BDE-77S was used as an internal standard, and 4 concentrations were prepared for it (ng/µl): 0.2505, 0.501, 1.002 and 2.505. Each concentration was injected 3 times into a GC-µECD, which gives a response in Hertz (Hz), and then the values were averaged out. Table 9 shows the current calibration values for the PBDEs. Most calibration points showed a small coefficient of variance (≤4%), except on the case of very small concentration (≤10%), and the correlation coefficients from signal response to injected amount for most of the PBDEs showed a strong relationship ($R^2 \geq 0.98$) from the concentration prepared.

Two compounds that showed a behavior not so stable are BDE-190 and BDE-209. These two compounds have heavy molecular weights, and become more problematic to detect with the

current set-up. Even under said issue, the correlation coefficient should be sufficient for its detection.

PBDE	Slope (ng/Hz)	R^2
BDE-17	54124.81	0.9918
BDE-28	61528.1	0.9887
BDE-47	58518.38	0.9885
BDE-66	62415.06	0.9881
BDE-71	65464.24	0.9889
BDE-77S	31092.62	0.9909
BDE-85	60328.88	0.9836
BDE-99	62878.74	0.9824
BDE-100	60495.72	0.9908
BDE-138	60632.29	0.9803
BDE-153	63861.8	0.9821
BDE-154	60298.09	0.9879
BDE-183	58104.07	0.9823
BDE-190	25835.93	0.9531
BDE-209	13630.27	0.8748

Table 9: Calibration of PBDEs with slope and correlation coefficient

RECOVERY RATIO

To determine the actual amount of chemicals that transferred from the PUF cartridge to the amber flask, recovery ratios must be determined.

A PUF cartridge was placed into a clean glass flask and sonicated with 100 ml of Hexane 4 times. This PUF is then injected with 30 µl of a 200 µg/ml 6 phthalates standard, 30 µl of a 5 µg/ml 13-PBDEs standard, 30 µl of a 24.62 µg/ml BDE-209 standard and 20 µl of a 50.1 µg/ml standard of BDE-77S.

Recovery ratios for the 21 compounds were determined with the help of MS Excel and are shown in Table 10 and Table 11.

Phthalate	Recovery Ratio
DMP	83%
DEP	77%
DBP	82%
BBP	92%
DEHP	77%
DoP	77%

Table 10: Recovery Ratio for Phthalates

PBDE	Recovery Ratio
BDE-17	84%
BDE-28	84%
BDE-47	84%
BDE-66	83%
BDE-71	80%
BDE-77S	84%
BDE-85	82%
BDE-99	82%
BDE-100	80%
BDE-138	80%
BDE-153	80%
BDE-154	78%
BDE-183	82%
BDE-190	77%
BDE-209	84%

Table 11: Recovery Ratio for PBDEs

ANALYSIS AND EXTRACTION

SORBENT TUBES

Phthalate samples collected for the first 7 test sites were collected using two sorbent tubes packed with Tenax TA. The two tubes were connected in series creating to monitor any breakthrough of the sorbate unto the sorbent. Duplicate sample trains were collected for tests 2, 3, 4, 5, 6 and 7. Neither calibration check nor internal standard were used for sorbent tubes, so an uncertainty of 100% is assumed. The relative variance between the replicate samples was

calculated for all 6 phthalates monitored for this study using Equation 1. The results of these calculations along with the cumulative statistics for the calculations can be found in Table 12. In general, the relative percent difference observed for sorbent tubes were well within the uncertainty of ±100%. There are, however, two site-SVOC category combinations with a relative % variance greater than ±100%. The elevated uncertainty resulted from a calculation in which one sample train showed a low mass concentration for the SVOC and the replicate sample train was non-detect. By convention, calculation of relative variance for non-detect sorbent tube assumes a value of 50% of the detection level for the non-detect value. Such calculations are subject to large uncertainties.

$$\text{Relative variance} = \frac{\left|rep1 - rep2\right|}{\frac{rep1 + rep2}{2}} \times 100 \quad (1)$$

Where:

rep1 = the cumulative mass concentration for a SVOC measured in sampling train 1; , and

rep2 = the cumulative molar concentration for a SVOC measured in sampling train 2;.

If rep1=0 and rep2≠0, rep1 is replaced by half the detection limit (5 ng);).

If rep1=0 and rep2=0, the relative variance is replaced by non-detect (ND).

PUF tubes

Phthalate and PBDE samples for tests 14, 15, 17, 19, 20, 21, 22, 23 and 24 were collected using tubes with polyurethane foam (PUF). Prior to sampling, a blank PUF tube was injected with a known mass of all the target phthalates and PDBEs to determine the recovery ratio of each compound. The recovery ratio for all compounds was on average 81%, with a range of 77 to 92% for all compounds. BDE-77S, a PBDE not found in indoor environments, was used as an internal standard to check for the sample processing uncertainty. Recovery ratios for BDE-77s fell was on average 74%, with a coefficient of variance of 22%. A calibration standard was also run prior to each GC injection. The coefficient of variance for the calibration standards always

was below 10% of for all injections. The overall uncertainty for analytical procedure was calculated from the first rule of combination (square root of the sums of squares) of each uncertainty using Equation 2.

$$\mu_c(C_A) = C_A\sqrt{\left(\frac{\mu_r}{R}\right)^2 + \left(\frac{\mu_{sp}}{V}\right)^2 + \left(\frac{\mu_{pc}}{C_A}\right)^2 + \left(\frac{\mu_{cc}}{C_A}\right)^2} \quad (2)$$

where:

$\mu_C(C_A)$ = the combined mass concentration uncertainty for a SVOC,;

C_A = the mass concentration for a SVOC [µg/m^3 for phthalates, ng/m^3 for PBDEs],;

μ_r = the uncertainty associated with the recovery ratio [%],;

R = recovery Ratio [%],;

μ_{sp} = the uncertainty associated with the sample processing [µl],;

V = volume [µl],;

μ_{pc} = uncertainty associated with the preparation of the calibration solutions [µg/m^3 for phthalates, ng/m^3 for PBDEs], and;

μ_{pc} = uncertainty associated with the calibration check [µg/m^3 for phthalates, ng/m^3 for PBDEs].

Duplicate sample trains were collected for tests 14, 15, 17, 20, 21, 23, 24. The relative variance between the replicate samples was calculated for all 6 phthalates and 14 PBDEs monitored for this study using Equation 3.26. The results of these calculations along with the cumulative statistics for the calculations can be found in Table 13. In general, the relative percent difference observed for PUFs were well within an uncertainty of ±100%. There are, however, thirty seven site-SVOC category combinations (33% from total) with a relative % percent variance greater than ±100%. The elevated uncertainty resulted from a calculation in which one sample train showed a low mass concentration for the SVOC and the replicate sample train was non-detect. By convention, calculation of relative variance for non-detect PUF tubes assumes a

value of 50% of the detection level for the non-detect value. Such calculations are subject to large uncertainties.

								Cumulative Statistics			
Test	**Site**	**DMP**	**DEP**	**DBP**	**BBP**	**DEHP**	**DoP**	**Mean**	**SD**	**Min**	**Max**
HaT	2	ND	26.3	40.9	12.9	104.5	49.2	46.8	35.1	12.9	104.5
MbT1	3-1	16.1	29.9	16.5	ND	125.8	ND	47.1	52.9	16.1	125.8
MbT1	3-2	8.2	6.4	19.3	ND	41.6	ND	18.9	16.2	6.4	41.6
ScP	4	22.8	20.0	25.3	22.7	13.2	ND	20.8	4.6	13.2	25.3
SdT	5	5.7	7.9	17.3	6.1	33.3	ND	14.1	11.7	5.7	33.3
GeT1	6	59.2	61.3	70.1	88.9	86.8	ND	73.3	13.9	59.2	88.9
MbP1	7	19.1	11.5	0.3	ND	20.4	ND	12.8	9.2	0.3	20.4

Table 12: Relative variance [%] between SVOC concentrations in replicate sorbent tubes

																						Cumulative Statistics			
Test	**Site**	**DMP**	**DEP**	**DBP**	**BBP**	**DEHP**	**DoP**	**BDE-17**	**BDE-28**	**BDE-47**	**BDE-66**	**BDE-71**	**BDE-85**	**BDE-99**	**BDE-100**	**BDE-138**	**BDE-153**	**BDE-154**	**BDE-183**	**BDE-190**	**BDE-209**	**Mean**	**SD**	**Min**	**Max**
14	EgP1	13.3	10.0	17.6	6.0	1.6	5.6	58.0	80.1	173.5	131.4	145.2	197.9	165.6	104.8	196.4	197.7	195.7	59.1	194.5	49.7	100.2	77.9	1.6	197.9
15	FfT2	43.9	18.7	4.6	25.7	7.5	29.9	39.2	29.4	19.9	10.9	199.4	69.9	133.8	31.2	95.6	84.6	190.7	128.8	72.6	81.1	65.9	58.3	4.6	199.4
17	MbP3	9.6	7.6	1.2	118.2	12.3	48.7	40.7	8.1	ND	10.5	89.9	15.2	7.2	45.2	0.4	2.1	4.7	34.2	22.6	8.7	25.6	31.8	0.4	118.2
20	EgP2	ND	11.0	51.7	1.7	0.4	72.5	ND	19.8	199.7	41.3	199.4	65.0	76.3	187.0	129.5	15.0	ND	117.1	30.6	18.0	72.7	69.3	0.4	199.7
21	GeP	ND	11.0	51.7	1.7	0.4	72.5	48.9	106.5	ND	ND	50.0	199.3	109.5	9.7	26.1	15.1	10.2	ND	30.2	ND	49.5	54.3	0.4	199.3
23	MiPI	ND	0.7	19.4	ND	9.1	ND	5.0	62.0	41.7	33.7	ND	37.4	ND	ND	106.5	58.7	1.2	84.0	ND	27.5	37.4	32.9	0.7	106.5
24-1	MiTI	20.2	27.0	68.2	41.0	40.5	ND	117.4	199.6	ND	122.6	ND	199.1	ND	96.0	198.0	16.8	198.9	21.4	188.4	50.2	100.3	74.4	16.8	199.6
24-2	MiT	ND	56.4	18.9	5.7	79.8	ND	9.1	3.6	199.9	148.5	ND	199.8	199.1	ND	156.4	11.1	ND	199.3	37.3	ND	94.6	84.1	3.6	199.9

Table 13: Relative variance [%] between SVOC concentrations in replicate PUF tubes

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Vita

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